44th Oilseed Conference

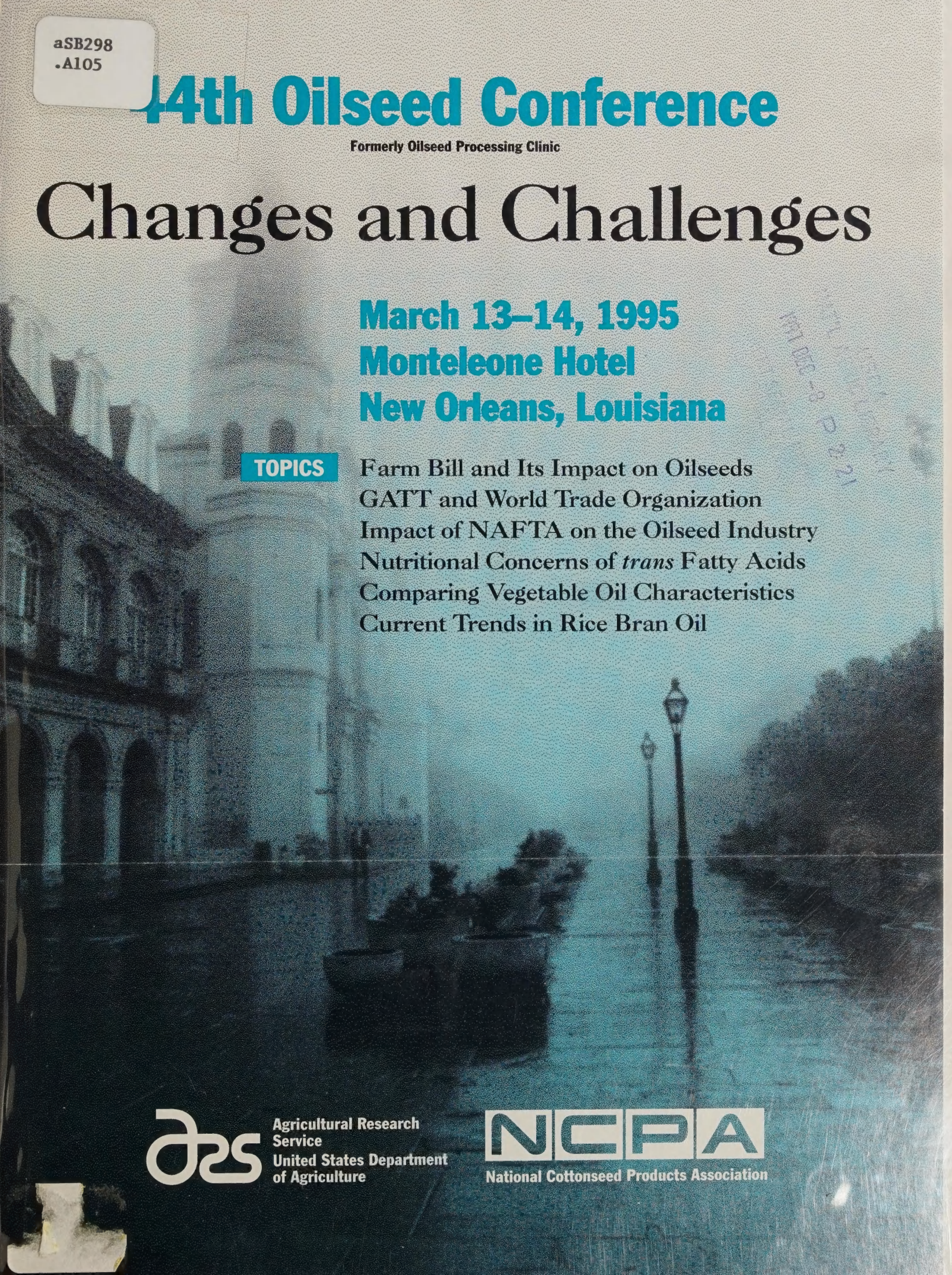
Formerly Oilseed Processing Clinic

Changes and Challenges

March 13–14, 1995
Monteleone Hotel
New Orleans, Louisiana

TOPICS

Farm Bill and Its Impact on Oilseeds
GATT and World Trade Organization
Impact of NAFTA on the Oilseed Industry
Nutritional Concerns of *trans* Fatty Acids
Comparing Vegetable Oil Characteristics
Current Trends in Rice Bran Oil



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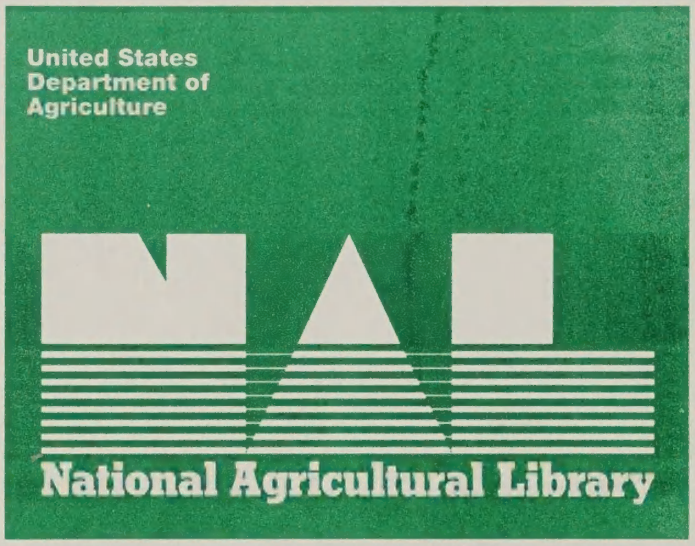
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PROCEEDINGS OF

44TH OILSEED CONFERENCE
(Previously called Oilseed Processing Clinic)

'CHANGES AND CHALLENGES'

MARCH 13-14, 1995

Monteleone Hotel
New Orleans, Louisiana

Sponsored by:

NATIONAL COTTONSEED PRODUCTS ASSOCIATION
and
SOUTHERN REGIONAL RESEARCH CENTER
AGRICULTURAL RESEARCH SERVICE
U.S. DEPARTMENT OF AGRICULTURE

DEDICATION

This Conference (previously called Oilseed Processing Clinic) is dedicated to the late DR. JOHN A. BARKATE who served as the Associate Director of the Southern Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture from 1983 until 1987, and as Director from 1987 until the time of his death in April of 1994. Dr. Barkate will be remembered by many in the oilseed industry for his commitment to the Center's research on oilseeds and for his strong support of the annual "Clinic."

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MONTELEONE HOTEL
NEW ORLEANS, LOUISIANA
MARCH 13-14, 1995

"CHANGES AND CHALLENGES"

Monday Morning, March 13, 1995

INVOCATION

Don W. Oliver
Linter Purchasing Manager
Buckeye Cellulose Corp.
Memphis, Tennessee

CALL TO ORDER BY GENERAL CHAIRMAN

Bill Quattlebaum
Manager
Southern Cotton Oil Company
Division of ADM
Lubbock, Texas
(Vice President, National Cottonseed Products Assn.)

WELCOME

John Patrick Jordan
Director
Southern Regional Research Center*
New Orleans, Louisiana

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William G. Clark
Executive Vice President and General Manager
Yazoo Valley Oil Mill, Inc.
Greenwood, Mississippi
(President, National Cottonseed Products Assn.)

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Miles M. Goggans
President
Goggans, Inc.
Little Rock, Arkansas

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Senior Vice President and General Manager
Plains Coop Oil Mill
Lubbock, Texas

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Gary W. Williams
Professor, Agricultural Economics
and
Director, Texas Agricultural Market Research Center
Texas A&M University
College Station, Texas

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Oilseeds and Products Division
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U.S. Department of Agriculture
Washington, D.C.

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Michael K. Dowd
Food and Feed Processing Research
Southern Regional Research Center*
New Orleans, Louisiana

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J. Berrye Worsham, III
Director
Market Research and Business Information
Cotton Incorporated
Raleigh, North Carolina

RESEARCH PRIORITIES AT ARS

Wilda H. Martinez
Deputy Associate Administrator
Agriproducts and Human Nutrition Research
National Program Staff*
Beltsville, Maryland

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President and General Manager
Osceola Products Company
Osceola, Arkansas

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Director of R&D
Anderson International
Cleveland, Ohio

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Research Leader
Diet and Human Performance Laboratory*
Beltsville, Maryland

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Frito Lay, Inc.
Plano, Texas

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Professor and Director
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Texas A&M University
College Station, Texas

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Southern Regional Research Center*
New Orleans, Louisiana

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Commodity Safety Research
Southern Regional Research Center*
New Orleans, Louisiana

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Manager, Operating Services
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Chandler, Arizona
(Chairman, Alternate Solvents Task Force)

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Phillips Petroleum Company
Bartlesville, Oklahoma

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Food and Feed Processing Research
Southern Regional Research Center*
New Orleans, Louisiana

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R. W. Emerson
North America Sales Manager
Specialty Chemicals
Phillips Chemical Company
Division of Phillips Petroleum Company
Bartlesville, Oklahoma

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R. W. Emerson and B. A. Todd
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Bartlesville, Oklahoma

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New Orleans, Louisiana
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Southern Regional Research Center*
New Orleans, Louisiana

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C. A. Bailey, Department of Poultry Science
H. L. Kim, Department of Physiology and Pharmacology
Texas A&M University
College Station, Texas
and
P. J. Wan
Food and Feed Processing
Southern Regional Research Center*
New Orleans, Louisiana

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*AGRICULTURAL RESEARCH SERVICE
U.S. DEPARTMENT OF AGRICULTURE

ADVANCEMENT OF PROCESSING HARDWARE

by

MAURICE A. WILLIAMS
DIRECTOR R&D
ANDERSON INTERNATIONAL CORP
CLEVELAND, OHIO

Two adaptations of expanders have improved oilseed preparation: one in solvent plants, the other in fullpress plants. The one for solvent plants is a hydraulic cone choke to replace the die plate. The second adaptation replaces the expander's die head with a shearcone and adjustable shearing jaws. Running with no injection of steam and allowing the shaft, cone, and jaws to shear the oilseed, this modified "DOX" Expander can pulverize the oilseed, rupture the oil cells, cook to harden protein, and flash off some of the natural moisture. The result is an inexpensive and effective way to pretreat oilseeds for fullpressing.

Expanders have revolutionized oilseed processing. Their ability to transform flakes, especially poor quality flakes and even fines, into porous collets has greatly simplified oilseed preparation. Expanders allow many processors to increase plant capacity and improve solvent recovery. The addition of a drainage cage in 1991 allowed expanders to accept seeds of high oil content without prior deoiling. This enabled processors lacking screw presses to process high-oil materials on the same expander they use to make soybean or cottonseed collets.

Recent hardware modifications have adapted expanders for better utilization in solvent extraction plants and in fullpress crush plants. The hardware modifications are a hydraulically positioned cone choke to replace the traditional die plate for collet expanders in solvent extraction plants and an adjustable-jaw shearing mechanism to adapt an expander for low moisture extrusion preparation in a fullpress crush mill.

Hydraulically Positioned Cone Coke.

Die plates do a fine job forming collets if the expander remains in steady-state operation. But if feed flow or feed quality fluctuates, the pressure generated by the expander fluctuates also. This results in fluctuations in motor load, collet firmness, internal porosity, etc. The only remedy for this situation is to correct feed flow fluctuation. To do so is sometimes extremely difficult, especially on machines run with minimal operator attention.

A hydraulically positioned cone choke, unlike a die plate, can automatically reposition itself in response to pressure changes within the expander. This compensates for the pressure changes and tends to keep the expander operating at uniform pressure even if there is some fluctuation in the incoming feed. Uniform pressure helps to keep product firmness and product porosity uniform.

Another advantage of a hydraulically positioned cone compared to a die plate is that a cone can be opened more than usual when starting up on fresh material and then closed more tightly when the expander becomes hot and softens the oilseed. Some oilseeds containing hulls, for example, are difficult to start up using small dies, but when the expander reaches operating temperature, the dies suitable for start up are now too large. Collet quality, then is not as good as it would have been if smaller dies could have been used.

A third advantage of a hydraulically position cone concerns purging and cleaning the expander on start up and shut down. A die plate has to be unbolted from the expander to change dies or clean out the expander. A hydraulically positioned cone is merely retracted to its full six inches of travel. The expander can then be emptied without unbolting anything.

The switch-over to mount the new choke is simple: remove the die plate and bolt on a replacement apparatus that consists of a housing containing the hydraulic cylinder, the positionable cone, and the ring against which the cone closes when the cone is moved fully closed. Then connect the hoses to the hydraulic power pack, and plug in the power cord.

Product from the expander flows between the inner surface of the ring and the outer surface of the cone. The product looks like a cylindrical sheet of material flowing over the cone. The sheet splits right away and falls apart into 1/2 to 2 inch particles similar to the way continuous strands of products flowing through dies break apart into individual collets. The sheet of material puffs with internal pores similar to the way strands extruding through dies puff. The particles, whether they come from sheets over cones or strands through dies, have good internal porosity,

adequate strength not to disintegrate in the extractor, and can be extracted to low residual oil.

The cone can be positioned against the ring in one of two ways. One way is to rock a lever forward or backward and the cone moves toward or away from the ring until the lever is placed in an upright position. The hydraulic cylinder then locks the cone in that position, and the cone cannot move again until the lever is rocked away from the upright position.

The second way is to rock the lever forward and leave it there. The cone will then start to move toward the ring. (There is six inches of travel from full open to full closed position). If the expander is running, and product is flowing over the cone, the pressure inside the expander will increase as the cone closes. The force closing the cone is generated by the hydraulic cylinder. When the force exerted by the expander equals the force exerted by the hydraulic cylinder, the cone will stop closing. The cone is now in the "floating mode".

The force on the hydraulic cylinder is uniform because it is generated by hydraulic fluid under controlled pressure. If the force exerted by the expander increases or decreases due to any kind of fluctuation, the cone will move forward or backward until the force exerted by the expander equals the force exerted by the hydraulic cylinder. In this fashion the "floating mode" will automatically reposition the cone to maintain a uniform pressure within the expander.

That pressure can be adjusted by adjusting the knob controlling the pressure of the hydraulic fluid. The hydraulic pressure can be adjusted from zero psi to 1500 psi. The ratio of areas between the hydraulic ram and the cone point is 0.62. The pressure inside the expander, therefore, is 62% of the hydraulic pressure.

Adjustable-jaw expander

So far, we have been discussing expanders to prepare oilseeds ahead of solvent extraction. These expanders: (1) make collets from flakes or prepressed cake, (2) make collets directly from high oil materials, (3) use die plates or hydraulic cone chokes. They are operated to: (1) produce collets with porous internal structure to allow solvent to flow through the interior of the collets, (2) rupture almost all the oil cells so that the collets will extract to less than 1% residual oil, and (3) utilize injected steam to assist in the cook. The collets are always cooled (sometimes dried and cooled) to insure that the collets enter the extractor at about 9-10% H_2O and 130-160°F.

If an expander is used to prepare oilseeds for fullpressing, the requirements are different. A porous internal structure is not needed. It is undesirable to inject steam (or water) into the expander. The product need not be cooled but should lose enough moisture (by flashing) to enter the screw press at about 5-6% H_2O. Also, the requirement to rupture oil cells is not as stringent. Fullpress cake at about 5% residual oil is the target.

Expanders are modified for this application by reducing the channel depth and causing the product to flow over a rotating cone point and through adjustable jaws. Adjusting the jaws influences how much shear is generated by the expander, and this influences how thoroughly the oil cells are ruptured and how much frictional heat is generated. Whole, unheated oilseeds can be processed by the adjustable jaw expander, but cracking and pre-heating permits higher capacity. This adjustable-jaw expander is already operating on soybeans. Adding a drainage cage would adapt it for seeds of high oil content.

With soybean, the seed is cracked into 6 or 7 particles and heated to about 170°F. The moisture of the fresh bean should be no higher than 10%. If it is higher, especially if it's higher than 12%, a bean dryer should be used before the cracking rolls. The cracked, preheated bean enters the adjustable-jaw expander and is subjected to maceration and shear by the worms and the rotating cone. This pulverizes the bean, rupturing most of the oil cells and generating frictional heat.

The moisture of the bean influences the work done by the expander. If moisture is too high, not enough work and frictional heat is generated to adequately rupture oil cells and flash off moisture in route to the screw press. If moisture is too low, overheating would result, but this can be compensated for by injecting some live steam into the expander.

The product comes out of the expander as an oily meal with some of the natural moisture boiling through the oil. This makes the product appear frothy, almost fluid-like, until the forcible flashing of moisture has ceased. The desired amount of temperature generated by an expander preparing oilseeds for fullpressing is higher than that desired when preparing oilseeds for solvent extraction: 280°F compared to 235°F. This temperature is sufficient to denature the protein and inactivate enzymes. Urease and trypsin inhibitor in soybean, for example, are inactivated. The product from the adjustable-jaw expander, incidentally, can be cooled and bagged as full fat soy.

The lower temperature desired in an expander making collets for solvent extraction does not inactivate urease or trypsin inhibitor. But one can make full soy on a collet expander by grinding the beans, using smaller die openings, and injecting

enough live steam to raise the moisture to 18-20% and the temperature to 250-270°F. This higher-moisture, higher-temperature cook produces an excellent full fat soy, but the product exits as a meal rather than collets. Die plate expanders are used to make full fat soy in feed mills as well as soybean collets in solvent extraction plants.

The frothy, semi-fluid product from the adjustable-jaw expander loses a couple percentage points of moisture from flashing and several more percentage points by evaporation as the hot meal is conveyed to the screw press. The conveyors should permit the water vapor to escape before it can condense and drip back into the meal. Open-top conveyors, or preferably hooded conveyors with drafting ductwork, can allow the vapors to escape from the meal and be blown outside. The moisture should drop from 10% in the expander to 5-6% before entering the screw press. This is easily done. Usually an inclined screw conveyor serving an overhead cross conveyor to the screw press is sufficient.

Traditional preparation for fullpressing soybean calls for cracking and drying. Very little maceration or oil cell rupture occurs before the screw press. The screw press, itself, in a traditional soybean fullpress operation, generates the shear and friction. To do this, a shaft having narrow channel depth and capable of generating high pressure is used. To withstand the high degree of pulverization exerted by the shaft, the soybean is dried to 2-3% moisture.

Since the adjustable-jaw expander has already ruptured most of the oil cells, the screw press need not work so hard. A less severe shaft is used, having greater channel depth and turning at a faster speed. Higher moisture (5-6%) permits lower horsepower consumption. All of this allows a screw press to operate at 3 to 4 times its traditional capacity on soybean.

An adjustable-jaw expander can be equipped with a drainage cage. This would adapt it for use with seeds of high oil content. The seeds can be cracked or flaked, heated or unheated and pass directly into the expander. Some of the oil fully liberated within the expander escapes through the drainage cage. The solids, continue through the expander over the shearing device, out through the adjustable jaws, and continues on to the screw press. Oil from the expander cage is combined with oil from the screw press for subsequent processing.

Another use for this adjustable-jaw expander with drainage takes us back to preparation ahead of solvent extraction. This expander can be used in place of a stack cooker to pre-heat and cook oilseeds ahead of a screw press or ahead of a collet expander. The jaws are opened more than for preparation ahead of a fullpress and some live steam is injected. This reduces the shear and frictional heat and, therefore, permits much higher

capacity. What this machine does is provide a very rapid cook (10 to 20 seconds) compared to a conventional, atmospheric pressure cooker, which has a 20 to 40 minute residence time and usually takes 5 to 10 minutes to bring the incoming material to cooking temperature.

As a result, enzymes, which are activated when the seeds are flaked or cracked, have 5 to 10 minutes to damage the oil or protein before the oilseed reaches a high enough temperature to inactivate the enzymes. For example, canola contains enzymes that release phosphorous compounds into the oil. If canola is preheated in a conventional cooker, the crude oil contains 250-270 PPM phosphorous. If the canola is preheated in adjustable-jaw expander, the crude oil contains 30-40 PPM. There is also a reduction in chlorophyll content, free fatty acid, peroxide valve, and a noticeable reduction of the greenish hue due to chlorophyll. This improvement in oil quality is sufficient justification to prefer an adjustable-jaw expander over conventional cookers, but the small compact size of an expander compared to conventional cookers also makes the expander a better choice. In addition, the expander costs considerably less than an atmospheric cooker.

In summary, expanders have revolutionized the processing of oilseeds. A special modification has adapted expanders to process seeds of high oil content into extractable collets similar to collets from soybean and cottonseed. Another hardware modification has adapted expanders to maintain a steady pressure within the expander and to adjust the discharge opening while the expander is running. Still another hardware modification permits an expander to prepare cracked, unheated oilseeds for fullpressing without requiring a traditional cooker/dryer. Expanders have, and still are, revolutionizing oil seed processing.

COTTONSEED OIL ALTERNATIVES

BY
MONOJ K GUPTA
FRITO LAY INC., PLANO, TEXAS
PRESENTED AT THE 44TH ANNUAL MEETING, NEW ORLEANS
MARCH 12 - 14, 1995

Cottonseed oil has been the most recognized oil for cooking and frying purposes for decades. Potato chips manufacturers have regarded the oil as the **Gold standard,** because it produces a unique nutty, buttery flavored potato chips. When potato chips are fried in cottonseed oil and the product is packed in a gas barrier package under nitrogen flush, the product maintains its superior flavor for weeks or months depending upon the type of packaging material, degree of nitrogen flush and quality of the oil in which the product is fried.

While the consumer acceptance for cottonseed oil in fried potato chips is a definite plus, a new trend in the snack food industry is emerging rapidly, and posing a serious challenge to the cottonseed oil.

Nutritionists and the Consumer Advocates have been providing the consumers with the **"Good For You"** concepts, such as:

1. Food must be low in fat content.
2. Fat used in the food must be low in saturated fatty acids.
3. Oils, high in unsaturation is better.
4. Reduced daily consumption of fat is necessary.

As a result of this new awareness, there is a great deal of activity in the snack food industry to deliver products to the consumers that are:

1. Low in fat content.
2. Low in saturated fat.
3. Fat free.

Concepts 1 and 2 above have been pursued in various food products such as salad dressing, baked products, ready to serve frozen entrées, snack foods etc. Some of these products are reasonably palatable while the others are not. This is one of the reasons why these category of foods, especially the snack type has not increased in volume as rapidly as it was originally anticipated. Product taste, mouth feel and satisfaction are lacking in some of these products. Research work in this area has shown that this is quite a complex situation and needs to be understood better.

Processing snack foods with oils that are low in saturated fatty acids, do not appear to be as difficult because lower saturated fatty acids in the oil does not necessarily change the product texture or mouth feel. However, there are some instances where the snack food made with the oils lower in saturated fatty acids exhibit a different flavor character. This is not simply because of the lower saturated fat content of the oil. This is basically the effect of the oil type on specific snack food.

Cottonseed oil contains 26 - 27% saturated fatty acids. **Table-I** shows the saturated fatty acid contents of common vegetable oils that are used in the snack food industry. While cottonseed oil does not have the highest level of saturated fatty acid content, it is ranked third on the list as shown in the table. According to the definition of the **Food & Drug Administration (FDA)**, products claimed to be **"Low In Saturated Fat"** must contain less than one gram of saturated fat in a serving size of one ounce (28.4 grams), or must not exceed 2 grams of saturated fat in a serving size of 50 grams. This should include fat derived from all ingredients in the food.

Using the above guideline, the amount of total fat content and the level of saturated fat in potato chips can estimated for the serving size of one ounce (28.4 grams) of chips as shown below:

Typical oil content of potato chips	36%
Total oil in serving size of one ounce	28.4 g x 0.36 = 10.2g
Saturate fatty acid content in the Cottonseed oil	26
Grams of saturated fat per serving	10.2g x 0.26 = 2.65g

Therefore, this product does not meet the FDA guideline on low in saturated fat because it contains 2.65 grams instead of < 1.0 gram of saturated fat per serving of one . Using the same method of calculation, total fat saturated content per serving of potato chips were estimated for all types of oil. The estimated values are shown in **Table-II.** Results indicate that one can make "Low in saturated fat" claim in potato chips by using only four types of oil. They are:

1. Canola oil.
2. Low linolenic acid canola oil.
3. High oleic sunflower oil.
4. Low linolenic, low saturated fatty acid soybean oil.

In order to make the same claim using cottonseed oil in potato chips, the oil content of the product must be 13.6%. This makes the product unfeasible. **Table-III** shows the estimated oil contents in potato chips that would allow "low in saturated fat" claim on the product fried in these various types of oil.

As stated above, there are only four types of oil that could be used in potato chips if the product has to meet the low in saturated fat claim. Without the low in saturated fat claim, one could use corn oil in potato chips. Regular canola, soybean and sunflower oils need to be lightly hydrogenated before they can be used for frying. With hydrogenation and no FDA regulations on **Trans Fatty Acids** content of the oil, one could make a claim of low in saturated fat using lightly hydrogenated canola oil. However, there is a great deal of concern over trans fatty acids

Table I

Saturated Fatty Acid Content In Common Vegetable Oils

Type of Oil	% Saturated Fat Typical
Palm	63
Palmolein	45
Cottonseed	26
Corn	13.5
Soybean	15.3
Sunflower	12.7
Low Linolenic Acid Soybean	15.3
Canola	6.5
Low Linolenic, Low Saturated Acid Soybean	6.7
Low Linolenic Acid Canola	6.5
High Oleic Acid Sunflower	9.6

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Table II

Saturated Fat Content Per Serving Size
Potato Chips Fried In Different Types Of Oil

Type of Oil	Gms SaturatedFat/ Serving Size
Palm Oil	6.4
Palmolein	4.6
Cottonseed	2.7
Soybean	1.6
Corn	1.4
Sunflower	1.3
Low Linolenic Soybean	1.6
High Oleic Sunflower	0.98
Canola	0.7
Low Linolenic, Low Saturated Acid Soybean	0.7
Low Linolenic Acid Canola	0.7

Table III

Theoretical Oil Content of Potato Chips To Meet FDA Guideline of Low In Saturated Fat

Type of Oil	% Oil In Product/ Maximum
Palm Oil	5.6
Palmolein	7.7
Cottonseed	13.6
Soybean	22.3
Corn	25.6
Sunflower	27.7
High Oleic Sunflower	36
Canola	36
Low Linolenic, Low Saturated Acid Soybean	36
Low Linolenic Acid Canola	36

and their possible nutritional implications. This is another reason why the low linolenic acid canola oil and low linolenic, low saturated fatty acid soybean oil are becoming so important. Both of these oils contain less that 3% linolenic acid and do not require hydrogenation. Both have a total saturated fatty acid content of less than 7%.

Selection Criteria For Choosing An Alternative For Cottonseed Oil

Replacement of cottonseed oil in potato chips is not without significant challenge. The oil serves a major role in fried food. It provides the flavor, texture, mouthfeel and shelf life in the product. Therefore, a replacement oil must deliver the following:

1. Cost must be within reason.
2. The product must be at least equally acceptable as the current product to the consumers in flavor, texture, mouthfeel and after taste.
3. The product must meet the required shelf life.
4. There must be an adequate supply of the oil.

If one simply wants to reduce the saturated fat content in potato chips by 50% and not sacrifice any product attribute including shelf life, corn oil provides an excellent opportunity. Corn oil and cottonseed oil products are equally accepted by consumers for flavor. The oil supply has risen to 2 billion pounds and is expected to be 2.4 billion pounds by the year 2000. Cost of this oil has been historically higher than that of cottonseed oil. However, during 1993 and 1994, one could buy corn oil at a price even lower than that for soybean oil. This makes corn oil an interesting contender for replacement of cottonseed oil, if one simply wants to reduce the saturated fat content of the product without the claim on low in saturated fat in potato chips and change the product appeal to consumers. This should be viewed as an immediate area of concern for the cottonseed industry.

Other Specialty Oils

As mentioned earlier, the only oils that one could use in potato chips and still make a claim on low in saturated fat content in the product are:

1. Canola oil.
2. Low linolenic acid canola oil.
3. High oleic acid sunflower oil.
4. Low linolenic , low saturated fatty acid soybean oil.

Using the selection criteria described earlier, one can analyze the situations with each of the specialty oils, their performance in potato chips frying and make reasonable prognosis for their success.

Canola Oil

Growth of canola oil has been phenomenal in US. **Table-IV** shows the usage of canola oil in this country. Canola oil consumption has risen from 181 million pounds in 1986 to 1.5 billion pounds in 1994. This growth has primarily been driven by the claim that the oil has the lowest saturated fat content in the market. This poses threats to both cottonseed and soybean oil. Most of this oil came from Canada. In 1994, the total acreage for canola oil in US was around 350,000. In 1995, the acreage is expected to be 450,000.

High Oleic Acid Sunflower Oil

High oleic acid sunflower is grown in North Dakota, South Dakota, Minnesota and Kansas. About 250,000 acres were planted with this variety in 1994, providing roughly 125 million pounds of oil. Nearly 60 million pounds of it was sold for food use, 40 million pounds were used for oleo chemicals, leaving a surplus of nearly 25 million pounds. In 1995 the expected acreage is 200,000, producing approximately 100 million pounds of oil.

The oil produces potato chips with a flavor character like that of cottonseed oil. In spite of its performance, the oil has not been grown in large volume because the grower, SVO does not want to sell this oil at a commodity price. The crop also faces the usual challenge of high grower premium, competition from other crops in the area and lack of infrastructure needed for crushing and refining. This has made the oil less attractive over the years although it performs well in the finished product.

Low Linolenic Acid Canola Oil

This category of oil is growing quite rapidly in the US. Unlike canola, which is mostly imported from Canada, the low linolenic variety of canola seeds are being grown in US. A joint partnership between Du Pont , Intermountain Canola and Anheuser Bush has been working on this project for several years and have made it a successful venture. The partnership is planning to plant over 100,000 acres of specialty canola in US and several thousand acres in Canada in 1995. The seeds are grown primarily in The Dakotas, Minnesota, with some in Georgia and West Texas. Several different low linolenic varieties of canola are being grown by Intermountain Canola. However, the partnership agreement prohibits any other potato chip or tortilla chip manufacturer from using this oil. SVO produced over 100 million pounds of a similar oil in 1994 but does not plan to contract any acreage in 1995 for lack of interest from potential users. There are three companies that are planting specialty canola seeds in Canada. The exact acreage is unavailable but it is estimated to be around 50,000. Calgene is expected to plant 5000 acres in 1995 in the state of Georgia.

Specialty canola is experiencing some agronomic as well as and some logistic and economic challenges. It has to compete with other crops grown in the area. There is no infrastructure for the crop at present. The price is high because of low production volume and high cost of identity preserved processing.

Table IV

Growth of Canola Oil Usage in USA

Year	Usage, Millions of Pounds
1986	181
1987	261
1988	488
1989	510
1990	577
1991	801
1992	912
1993	1,157
1994	1,500

The oil produces potato chips with a clean flavor but it does not match cottonseed oil flavor. Both of these oils, high oleic acid sunflower and low linolenic acid canola are costly. Bulk price for high oleic acid sunflower oil is $0.55/# and that for low linolenic acid canola oil is $0.44/#. Cargill Oil, who owns Intermountain Canola Oil Co. and is also the marketing arm for the high oleic acid sunflower oil of SVO is predicting a long range price for both oils to be in the upper thirties. This will improve the cost picture and help industries to make the transition to these oils.

Low Linolenic Acid Soybean Oil

This variety is under development. Pioneer Hibred has an experimental variety that looks promising. It contains less than 7% total saturated fatty acid and less than 3% linolenic acid. The oil has not been tested yet. However, their low linolenic acid variety containing 15.3% saturated fatty acids performs like cottonseed oil in potato chips and like lightly hydrogenated soybean oil in tortilla chips. Thus, one could expect the low linolenic, low saturated fatty acid soybean oil would produce similar results.

The United Soybean Board has undertaken a very aggressive program to develop a healthy version of soybean. Genetic technology is already available and the work has begun. One can expect to see a fully established variety in 4 years and first commercialization of the same in 6 years. This program has the greatest potential for providing a healthy oil at the lowest cost since the infrastructure is already in place for growing the seeds and commercialization of the same.

It is quite possible that specialty soybean could be developed for a few more maturity zones in 10 - 12 years.

Discussion

The recent trend in the snack food industry is going to put cottonseed oil at a disadvantage simply because of its high saturated fatty acid content in spite of its superior performance in potato chips. If there is pressure to reduce the saturated fat in potato chips without having a claim on low in saturated fat, one can easily deliver a satisfactory product fried in corn oil. A former user of cottonseed oil, Anheuser Bush has been replacing cottonseed oil with the low linolenic acid canola oil and is claiming **"Lowest In Saturated Fat"** on their potato chips package.

Consumer awareness on fat nutrition is becoming more intense. Snack food manufacturers have to respond. Current alternatives, such as high oleic acid sunflower or low linolenic acid canola oil can produce potato chips with good flavor and low saturated fat content. High price, contractual agreement, agronomic as well as logistic challenges for growing these seeds have made the oil less available to the general snack food manufacturers. Cargill is looking into commercialization of these oils. Researchers are also investigating other varieties of low linolenic acid canola variety that would have less than 5% of total saturated fatty acids.

Low linolenic, low saturated fatty acid soybean is an emerging variety. The United Soybean Board has undertaken an aggressive program to commercialize this variety. One can expect to see the first commercial variety in one maturity zone in 4 - 6 years. An expansion over several maturity zones could take place within the next 12 years. This will provide a very stable oil with the flavor character needed for both potato chips and tortilla chips.

Conclusion

Cottonseed oil could lose its position against corn oil today, if a snack food industry wants to reduce the saturated fat level in the product without a claim on low in saturated fat. Low linolenic acid canola oil is expanding rapidly. Cargill might find a way to deliver both low linolenic acid canola high oleic acid sunflower oils at a substantially reduced cost. Low linolenic acid, low saturated fatty acid soybean has been placed under a strong developmental program and can become the largest source of healthy oil at most reasonable price. All of these activities indicate a strong change in the snack food for the future. Cottonseed oil industry needs to take a hard look at the new trend and decide on its own course of action. Finally, one should think of delivering the healthier cottonseed oil at an affordable price and not consider it to be a **Designer Cottonseed Oil,** that can be purchased at a high premium like the high oleic acid sunflower oil.

Recommendation

Cottonseed growers, plant breeders and the National Cottonseed Producers Association must take the challenge seriously because cottonseed oil is going to face the competition from the various healthy oils. Fat nutrition is the emerging trend and must be met with organized research to grow cottonseed with less than 7% saturated fatty acid content, like low linolenic acid canola or low linolenic acid, low saturated fatty acid soybean.

Csoa295

DETOXIFICATION OF OILSEED MEALS

by

Khee Choon Rhee
Director
Food Protein Research and Development Center
Texas A&M University
College Station, Texas

Abstract

Meals from many oilseeds often contain undesirable toxic and/or allergenic compounds which can reduce their values severely and limit their uses in feeds. To remedy these problems, a number of processes have been developed to remove the undesirable components from the meals through extraction or physical separation or to destroy them chemical so that the resulting products can be used safely as ingredients in compounded feeds for poultry, swine and cattle. Some of these new processes have been adapted already for commercial production of detoxified and deallergenated meals while others still remain to be proven for commercial applications.

Introduction

Feed meals can be contaminated with toxins, allergens and other antibiological factors before harvest as well as during harvesting and storage operations of the source crops. Once contamination has taken place, the hazard associated with the toxins, allergens and antibiological factors has to be removed before the product can safely be used as feed ingredients.

Any detoxification and/or deallergenation process must be technologically sound and economically feasible to have a practical application. Based on the criteria outlined by the Food and Agriculture Organization (FAO) (1-4) and other national and international organizations (5-7) for aflatoxin decontamination, an acceptable detoxification and/or deallergenation process must: destroy, inactivate, or remove the toxic and allergenic materials; not produce or leave toxic or carcinogenic/mutagenic residues in the final products or food products obtained from animals fed decontaminated feed; retain the nutritive value and acceptability of the product; not significantly alter important processing and functional properties; destroy fungal spores and mycelia which could, under favorable conditions, proliferate and form new toxins; and not adversely affect the environment. This paper will highlight a couple of gossypol and aflatoxin detoxification methods that have already been commercialized and a promising new method currently under development for gossypol extraction.

Gossypol Detoxification

Gossypol is known to be toxic to monogastric animals such as swine, poultry and rabbits, and young calves. Gossypol content of glanded (or traditional) cottonseed ranges 0.4-1.7% (or about 2.4-4.8% of the weight of dehulled cottonseed kernels) and varies with species and maturity of the balls. Raw cottonseed kernels may contain 0.6-2.0% free gossypol. The US Food and Drug Administration (FDA) limits the free gossypol content in food products and ingredients to 450 ppm while the Protein Advisory Group of the United Nations Food and Agriculture Organization and World Health Organization (FAO/WHO) has a guideline which limits the free gossypol to 600 ppm and the total gossypol to 12,000 ppm. Feed industry has its own guidelines for free gossypol levels, i.e., 100 ppm maximum for broilers and 40 ppm for laying hens (8). For these reasons, various attempts have been made to eliminate gossypol through breeding, to deactivate (or blind) it during processing, to remove it by extraction with polar solvents or by mechanical separation of gossypol-containing glands or to detoxify or destroy it by reacting with selected chemicals.

Elimination of Gossypol

The most desirable method of dealing with the gossypol problem is undoubtedly its elimination from cottonseed. The discovery and development of a new variety of cotton called "glandless" cotton was first reported in the late 1950's (9), and glandless cotton planting seeds were made available commercially in 1980 in Texas (10) and in Louisiana (11) under various labels.

Although there are a number of advantages for processing glandless cottonseed over glanded seed (12), cultivation of glandless cotton fell far shorter than originally expected for various agronomic as well as economic and cultural reasons. At present, only about 3,000 acres are devoted to glandless cotton cultivation in Texas, and this acreage is expected to increase to more than 7,000 acres in the next planting year (13). For the foreseeable future, the majority of glandless cottonseed production is expected to be used for various food applications (14).

Physical Separation

The use of physical separation method has been limited to remove small amounts of glanded cottonseeds contamination from large amounts of glandless cottonseeds using electronic sorters to prepare for low-gossypol food products and food ingredients.

Heat Treatment

Production of low free gossypol cottonseed meals are routinely accomplished commercially by treating defatted cottonseed meals with moist heat. This heat treatment is usually carried out with the addition of iron salts, such as ferrous sulfate, which bind the free gossypol in the feeds and render them biologically inactive. Gossypol reacts with ε-amino group of lysine and possibly

with arginine and cystine during heating (15). Application of moist heat during processing of cottonseed reduces free gossypol, but also decreases protein solubility and lysine availability.

Solvent Extraction

Extraction of cottonseed with commercial hexane removes a relatively small portion of the gossypol with oil. Other reported procedures for solvent extraction of gossypol with polar solvent include the use of aqueous acetone (16), a mixture of acetone, hexane and water (17), sequential extraction with hexane, aqueous acetone and anhydrous acetone (15), butanol-hydrochloric acid solution (18), methylene chloride (19), hexane acetic acid (20), a mixture of ethyl alcohol and hexane (21) and isopropyl alcohol (91%). Some of the earlier compounded data on free gossypol extraction by various organic solvents are shown in Table 1.

Table 1. Free gossypol contents of cottonseed meals extracted with selected solvents

Solvent	First Extraction (%)	Second Extraction (%)
Ethanol, 95%	0.067	0.031
Isopropanol, 91%	0.055	0.031
Ethanol:Hexane (v/v)		
0:100	0.083	----
10: 90	0.080	----
20: 80	0.062	0.013
30: 70	0.038	0.016
40: 60	0.053	0.013
60: 40	0.043	----

In addition, techniques have been developed to grind dried glanded cottonseed (less than 2% moisture) with hexane and then separate the intact heavier gossypol glands by liquid cyclone process (LCP) (22-25). An air classification method has also been developed to separate intact gossypol glands from ground solvent-extracted flour (26-28).

More recently, researchers at Texas A&M University (29) investigated the efficacy of gossypol extraction with hexane and isopropyl alcohol (IPA) from expanded collets and their effects on the plasma gossypol level of weaning pigs. Sample 1 was prepared by flaking cottonseed meal once to 0.012-0.015 inch, making collets using a Hive expander, extracting the collets with 96% IPA and desolventizing. A Solve expander was used to prepare sample 2. For sample 3, cottonseed meal was moistened and rolled, expanded in a Hive expander, extracted with hexane and desolventized with live steam injection. Sample 4 was prepared by expanding with a Solve expander. Sample 5 was prepared by flaking cottonseed meal once to 0.015 inch, expanding the flake using a Solve expander, extracting the collets with hexane and desolventizing

without live steam. The effects of these treatments on gossypol contents of extracted meals are shown in Table 2, performance in feeding weaning pigs in Table 3 and the plasma gossypol contents in Table 4.

Table 2. Gossypol contents of cottonseed meals prepared by extracting Hivex and Solvex expanded collets with isopropyl alcohol and hexane

Expander	Solvent	AOCS Free Gossypol (%)	Total Gossypol (%)			
			AOCS	HPLC	(+)	(-)
Hivex[1]	IPA	0.055	1.061	1.108	59.0	41.0
Solvex[2]	IPA	0.051	1.041	1.028	57.2	42.8
Hivex[3]	Hexane	0.080	1.092	0.989	56.2	43.8
Solvex[4]	Hexane	0.092	1.049	0.964	56.6	43.4
Solvex[5]	Hexane	0.152	1.091	1.078	57.1	42.9

[1-5]See text for processing conditions.

Table 3. Performance of weaned pigs fed diets containing cottonseed meals prepared by extracting Hivex and Solvex expanded collets with isopropyl alcohol and hexane

Expander	Solvent	Feed (lb/day)	Gain (lb/day)	Feed/Gain
Hivex[1]	IPA	2.32	1.13	2.06
Solvex[2]	IPA	2.33	1.13	2.08
Hivex[3]	Hexane	2.22	1.02	2.18
Solvex[4]	Hexane	2.20	0.97	2.28
Solvex[5]	Hexane	2.26	1.07	2.13

[1-5]See text for processing conditions.

Chemical Inactivation

Chemical detoxification of gossypol in glanded cottonseed meals has been the subject of numerous investigations over the past several decades. There are more than two dozen different

methods have been proposed; however, for one reason or another, most of these methods have been unsatisfactory or impractical on a technological or economic basis or both (30). A series of new methods which utilize extruders as high temperature chemical reactors in the presence of selected chemicals, such as aminopropanol, ammonia, a mixture of sodium hypochlorite and ammonium sulfate or a mixture of urea and ferrous sulfate, seem very promising both technologically and economically.

Table 4. Total, (+) and (-) gossypol in plasma of weaning pigs fed diets containing cottonseed meals prepared by extracting Hivex and Solvex expanded collets with isopropyl alcohol and hexane

Expander	Solvent	AOCS Total Gossypol (%)	Gossypol Isomers (%)			
			(+)	% of Total	(-)	% of Total
Hivex[1]	IPA	0.064	0.040	62.7	0.024	37.3
Solvex[2]	IPA	0.074	0.045	62.7	0.029	37.3
Hivex[3]	Hexane	0.072	0.045	63.2	0.026	36.8
Solvex[4]	Hexane	0.058	0.036	62.1	0.022	37.9
Solvex[5]	Hexane	0.096	0.061	63.3	0.035	36.7

[1-5]See text for processing conditions.

This new process is simple to use (Figure 1), but very effective in destroying gossypol in cottonseed meals, as shown in Table 5. Animal feeding tests utilizing growing pigs indicated that the chemically treated cottonseed meals performed satisfactorily (about 95% of the growth rate of soybean meal fed pigs) and exhibited no detectable toxicosis or liver damage.

Table 5. Free gossypol contents of chemically treated and extruded cottonseed meals

Chemical	Free Gossypol, ppm	% Reduction
Aminopropanol, 2%	less than 50	99+
Ammonia, 4%	450	95+
Urea + Ferrous sulfate, 1.5% each	312	97+
Sodium hypochlorite + Ammonium sulfate, 1.5% each	less than 30	99+

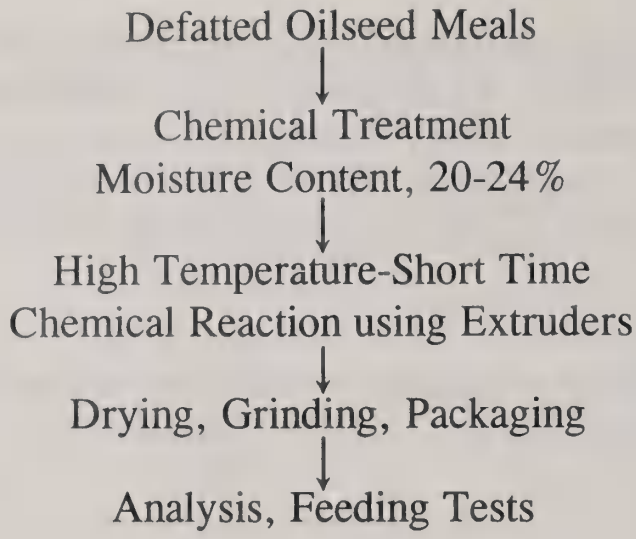

Figure 1. Processing steps involved in detoxifying oilseed meals.

Aflatoxin Detoxification

Peanuts and cottonseeds are the two oilseeds most susceptible to aflatoxin contamination. From the time the carcinogenic potential of aflatoxin was established, considerable attention has been focused on the removal and destruction of aflatoxins. As a result, numerous methods and procedures have been proposed on physical removal, solvent extraction or chemical inactivation of aflatoxins from these commodities and others (31-38). Physical removal of immature, damaged and discolored peanuts has been the technique rather successfully used by the peanut industry, but such techniques are not practical for cottonseeds or corn. Physical removal may not effectively detoxify these materials because aflatoxins diffuse away from the mycelia, and products with no visible evidence of mold damage can contain significant levels of aflatoxins (39). Various organic solvents and their mixtures were also used to selectively extract aflatoxins from peanut and cottonseed meals. While some of these procedures were quite effective in removing aflatoxins, none of these methods has been adapted for commercial applications due to various adverse effects, i.e., undesirable odor, safety, solvent recovery, expense, and others.

The most common as well as commercially successful aflatoxin detoxification techniques available today are the chemical methods utilizing various forms of ammonia and/or oxidizing agents under closely controlled processing conditions.

Ammoniation Procedures

In the United States, ammoniation procedures have been approved by selective states for use within those states. Arizona and California permit ammoniation of cottonseeds (40). Ammoniation has also been approved by several producer nations. A 100-ton capacity peanut meal ammoniation plant was built in Dakar, Senegal (5, 41-43). The plant capacity was

subsequently increased to 300 tons in 1983 and to 600 tons in 1984. Other ammoniation plants are known to operate in Zyginchor and Lyndiane in Senegal (43), Pontivy, near Brittany in France (44), and Port Sudan (45). France (46) and Canada (47) have also approved the ammoniation procedure.

Three types of ammoniation procedures are currently available: atmospheric pressure/ambient temperature, atmospheric pressure/high temperature; and high pressure/high temperature procedures. The effectiveness of ammoniation procedure is determined by (a) level of ammonia applied, (b) moisture level of the product being treated, © holding temperature, and (d) duration of exposure to ammonia (48).

Atmospheric Pressure/Ambient Temperature Procedure. This method, first developed by the U.S. Department of Agriculture, is the simplest procedure of all available methods (49). Defatted meals from peanuts and cottonseeds or whole cottonseeds are sprayed with ammonia, sealed the product in plastic bags, and stored at ambient temperatures. The typical reaction conditions reported are as follows: 0.5-4.0% ammonia; 12.5-22.5% moisture; 20-60°C reaction temperature; and 2-42 days of exposure. Under these conditions, reductions in aflatoxin levels ranging from 95% to 99% have been reported on peanut and cottonseed meals as well as on whole cottonseeds (Table 6) (50-57).

Table 6. Conditions used for ammoniation of peanut and cottonseed meals as well as whole cottonseeds and aflatoxin contents of products

Parameter	AP/AT	AP/HT	HP/HT
Ammonia (%)	1.5-4.0	3.0-4.0	1.5-4.0
Moisture (%)	15-30	17	5-15
Pressure (psi)	15-20	20-26	30-45
Temperature (°C)	10-40	100-125	80-150
Time	2-42 days	30-90 min	30-120 min
Reactor	Plastic bags	Pressure vessel	Pressure vessel
Capacity (tpd)	Variable	Variable	100-600
Aflatoxin (ppb)	less than 20	32-112	less than 20-50

Atmospheric Pressure/High Temperature Procedure. A British patent was issued on a method developed by the Tropical Development and Research Institute in England (58, 59). As summarized in Table 6, this method is also quite effective in destroying aflatoxin in peanut and cottonseed meals and whole cottonseeds. This method, however, requires external source of heat and reaction vessels to raise and maintain the reaction temperature at desired levels.

High-Pressure/High-Temperature Procedure. The use of anhydrous ammonia under high pressure and temperature to detoxify aflatoxin in peanut meal was reported as early as in 1968

(60), a patent was issued in the following year (61), and pilot as well as production scale testings on peanut and cottonseed meals as well as whole cottonseeds were carried out from the early 70's to mid 80's (62-68). This method is quite effective in destroying aflatoxins (Table 6), but requires reaction vessels which can withstand both high temperatures and pressures needed for the detoxification reaction.

Ammoniation can alter the composition and characteristics of feeds or feed ingredients. The most common alterations reported include increased levels of total nitrogen (48, 51, 63, 66, 69-72), nonprotein nitrogen (35, 48, 52, 66), and soluble solids (48). Reductions in cystine and methionine (33, 63, 70, 73) and nonreducing sugar (48, 70) levels, and nitrogen solubility index (6, 35, 63-66, 72) were also reported.

Animal feeding studies revealed that the ammonia detoxified meals produced no observable signs of aflatoxicosis or liver damage in the ducklings (35, 60, 63), rats (4, 52, 63), trout (51), and food-producing animals (52, 57, 62, 74-77). Also, they had no significant effect on body weight and feed efficiency (78). There were however some reductions in protein efficiency ratio, nitrogen solubility and lysine availability .

Chemical Treatment and Extrusion Procedures

Aflatoxin contaminated oilseed meals can also effectively be detoxified by first treating them with selective chemicals and then passing the mixtures through an extruder or expander at elevated temperatures (79). In these procedures, the extruder or expander acts as a continuous, high temperature, high pressure chemical reactor as well as a production equipment.

Briefly, the contaminated meal is mixed with chemicals (1-2% total concentration) and water to a final moisture content of about 24%. After equilibration (about 30 minutes of continuous mixing), the chemically treated meal is extruded with an exit temperature of approximately 140-160°C. Live steam may be injected directly into the extruder barrel, if desired, to aid in maintaining the moisture level and reaction temperature in the barrel. The extrudates (or collets) are cut into 2.5-5.0 cm length, dried, ground and packaged for further handling (Figure 1). Among the chemicals tested, the mixtures of sodium hypochlorite and sodium hydroxide (1% each) and sodium hypochlorite and ammonia (1 and 4%, respectively) were found to be most effective in destroying aflatoxins. Under these conditions, aflatoxin contents of peanut and cottonseed meals can be reduced from about 300 ppb to less than 10-20 ppb for sodium hypochlorite/sodium hydroxide mixture and to less than 10 ppb for sodium hypochlorite/ammonia mixture, using a variety of extruders (including the Anderson 4.5" and 8" models and Wenger models X-20, X-25, X-175 and X-200).

Animal feeding studies on cattle, poultry and swine indicated that there are no signs for aflatoxicosis or liver damage on these animals when fed at 50% replacement of diets with treated peanut meal. Also, no significant difference was observed on body weight gain, feed efficiency and egg production. However, like the ammoniation procedure, there was a slight decrease in

protein efficiency ratio.

Currently, one peanut meal treatment facility is in operation in Diobel, Senegal with a rated total processing capacity of 27,000 lbs per hour using two units of Wenger X-200 extruders.

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NEW USES FOR OILSEED BY-PRODUCTS: TOXIC METAL ADSORBENTS FOR THE FUTURE?

by

Wayne E. Marshall
Research Chemist
USDA, ARS, Southern Regional Research Center
New Orleans, Louisiana

and

Mitchell M. Johns
Research Assistant Professor
Department of Food Science, Louisiana State University
Baton Rouge, Louisiana

Cottonseed and soybean hulls are low value, high volume by-products from two crops of great economic value in the United States. Their current value resides largely as ingredients in animal feed but researchers at the Southern Regional Research Center have discovered their heretofore untapped potential as adsorbents for toxic metals commonly found in industrial and municipal wastewater. Two types of adsorbents, non-pyrolyzed and pyrolyzed, have been developed. Non-pyrolyzed adsorbents are simple to manufacture and at low cost, are efficient and effective at removing metals, but are normally limited to a single use. Pyrolyzed adsorbents, also known as activated carbon, are more costly to manufacture, are also quite efficient at metals removal and are multiple use adsorbents. The development and application of these adsorbents will be discussed along with their potential marketability as competitive commercial products.

Introduction

This report presents the current status of our research to convert the low cost, high volume agricultural by-products, cottonseed and soybean hulls into value-added products. Our objective is to develop non-pyrolyzed and pyrolyzed adsorbents which are competitive with similar commercial adsorbents in terms of their cost and effectiveness in removing metals at potentially toxic concentrations from wastewater.

Need for metals removal

Metals removal from industrial waste effluent and municipal drinking water sources is a serious and ongoing problem thoughout the United States. Metals removal has been a

problem of particularly large magnitude in the Midwest and South because of the region's vast water resources, large numbers of manufacturing and chemical industries and centers of high population density. The region, therefore, has a great potential for wastewater contamination from metals, among other pollutants. For example, metal comtaminants from the heavily industrial corridor between St. Louis, MO and New Orleans, LA can be leached or discharged into the Mississippi River. This is a problem of great concern to the industries which discharge the metals and to nearby municipalities which obtain their drinking water from surface water sources.

Methods of metals removal

In order to minimize metal pollution of surface waters and drinking water, industries and municipalities take preventive measures to physically or chemically remove these metals. Two widely used chemical methods depend on surface adsorption of a metal to a solid, and are ion-exchange and adsorption.

Ion-exchange methods for metal removal utilize a cation-exchange group of resins. This group includes a subgroup called chelating resins. Cation-exchange resins normally have a high capacity for metals. Many of the chelating resins are also highly selective for specific metals. Most commercial resins are petroleum derived, styrene-divinylbenzene-based copolymers with anionic functional groups covalently attached to the styrene-divinylbenzene matrix. Since they are synthetic materials, these resins are very durable and can undergo many regeneration (adsorption/desorption) cycles before they are discarded. However, these resins depend on petroleum for their manufacture. From an environmental standpoint, petroleum is a non-renewable resource, which is being depleted, not only in the United States but also worldwide.

Adsorption methods utilize activated carbon, usually in the granular form. Granular activated carbon (GAC) has a history of use in both air and water applications for the removal of organic substances which cause off-odors or off-flavors. The use of GACs for metal adsorption is a new applications area which is currently under development. A few metal-adsorbing GACs are commercially available but their adsorption capacity and metal selectivity are limited. Commercial GACs recommended by the manufacturer for metals adsorption use bituminous or lignite coal, coconut hulls or extruded peat as base materials. Bituminous and lignite coal are both non-renewable resources, rapidly being depleted in the United States. GACs can also undergo several regeneration cycles but are not as durable as cation-exchange resins.

Adsorbent availability and cost

Cottonseed and soybeans are commodities of great economic value in the United States primarily due to the large volume of oil extracted from them. For the 1993/1994 crop year, 12,700 and 112,500 million lbs of cottonseed and soybeans, respectively, were harvested (USDA, 1994). Before the seeds are crushed, they are dehulled. The resulting

hulls comprise about 26 and 8% of the total weight of cottonseed and soybeans, respectively. Therefore, 3,300 and 9,000 million lbs of cottonseed and soybean hulls, respectively, were produced in the United States (Table 1). Cottonseed and soybean hulls are considered low value by-products which are used in animal feed formulations. Their value fluctuates depending upon market demand, with cottonseed hulls commanding between $20-40 per ton and soybean hulls priced at $60-90 per ton. Soybean hulls have a higher protein content (8-10%, dry weight basis) than cottonseed hulls (2-4%, dry weight basis) and can demand a higher price when used in feed.

The availability of cottonseed and soybean hulls is much greater than for cation-exchange resins (Anonymous, 1994d) and their cost as an adsorbent is considerably lower (Table 1). The cost for hulls as adsorbents is based on estimated preparation (washing and drying) costs and bulk transportation costs from the oilseed crushing facility to the customer. The price range for cation-exchange resins is very broad (Anonymous, 1993) and includes a wide variety of commercial resins sold in bulk. The specialty resins, such as the chelation types, are at the high end of the price range.

The actual availability and cost of commercial GACs compared to the potential availability and estimated cost of converting cottonseed and soybean hulls to GACs are shown in Table 2. The availability of the commercial GACs (Anonymous, 1994a) is for all uses, not only metals, since data on the amount of activated carbon used strictly for metal adsorption was unavailable. The quantity of commercial GAC produced is only a fraction of the potential availability of GACs from cottonseed and soybean sources. Potential availability was calculated assuming all cottonseed and soybean hulls in the 1993/1994 crop year (Table 1) were converted to GACs at a 30% yield. The actual cost of commercial GACs represents the price range of GACs recommended for metals removal (Anonymous, 1994b; Anonymous, 1994c) and is higher than the estimated costs of the by-product-based GACs. These estimated costs were based on a pyrolysis and activation process which is less energy comsuming than the current commercial processes, thereby potentially making our activated carbons less costly to manufacture.

Non-pyrolyzed hulls as metal adsorbents

Our research program has evaluated cottonseed and soybean hulls in both their non-pyrolyzed and pyrolyzed forms as adsorbents for metals. As non-pyrolyzed by-products, hulls must possess three important characteristics to compete commercially as metal adsorbents: they must have sufficient adsorption capacity, adsorption efficiency and durability in the environment for which they are used.

These characteristics were compared to the commercial chelating resin Amberlite® IRC-718. IRC-718 was chosen because of its selectivity towards the metals chosen for evaluation. Table 3 shows the adsorption capacities (expressed as equivalents of metal adsorbed per lb of dry wgt) of IRC-718, cottonseed and soybean hulls for three metals commonly found in industrial and municipal wastewaters, namely zinc [Zn(II)], copper [Cu(II)] and nickel [Ni(II)] ions (Marshall and Champagne, 1995). Adsorption capacities for soybean and particularly cottonseed hulls were considerably less than for IRC-718.

However, IRC-718 is a relatively costly material with a current bulk price of $9.14 per lb. We have compared its cost to the estimated bulk costs of cottonseed and soybean hulls in their "ready to use" form (Table 1). Using these values, cost per equivalent of metal adsorbed was calculated. With Cu(II) as an example, the cost per equivalent of using cottonseed and soybean hulls are the same, but only about one-fourteenth the cost of using the commercial resin.

These cost comparisons are attractive from a by-product utilization standpoint. However, they do not tell the whole story. Adsorption efficiency, stability and regeneration properties must be considered before a decision to use a particular adsorbent can be made.

Adsorption efficiencies were measured by determining the percentage of metal removed from three different metal plating wastewaters (Table 4) (Marshall and Champagne, 1995). In all cases, IRC-718 removed more of the metals than the hull samples. Cottonseed and soybean hulls were only slightly less effective, generally removing 80-90% of the three metals. Both by-products had difficulty removing Zn(II) and Ni(II) from wastewater #1, were more effective in removing these metals from wastewater #2, and were most effective in removing all three metals from wastewater #3. The variability exhibited by cottonseed and soybean hulls, and to a lesser extent by the resin, for metal adsorption in "real world" wastewater samples is likely due to the presence of constituents other than metals. Industrial wastewater can be a complex mixture of both inorganic (including metals) and organic (detergents, lubricants) compounds. Other chemical species may either compete with metals for adsorption sites on the adsorbent's surface, or even complex the metals themselves. Based on this very small sampling of different wastewaters, the commercial resin may be expected to possess a greater efficiency in removing metals than the by-products. Further evaluations are required using a more comprehensive sampling of wastewaters.

When comparing adsorbents, the ability of the material to remain intact during a specific application is of critical importance. For example, if cottonseed or soybean hulls are labile, and hull components are leached away during use, then the adsorption properties of the hulls would be adversely affected. The hulls themselves would be a pollution problem, as the dissolved solids would have to be removed, probably by a separate treatment process.

For this study, the stability of cottonseed and soybean hulls were compared to the stability of IRC-718 in a batch adsorption process which employed mechanical stirring with a Teflon stir bar. Cottonseed and soybean hulls were found to have a higher percent of solids retained than either the commercial resin or two samples of rice bran added for comparison purposes (Table 5). Under the experimental conditions, cottonseed and soybean hulls were remarkably stable. If these results can be extrapolated to other batch processes, stability of these materials should not present a problem.

The regeneration properties of cottonseed and soybean hulls were evaluated. Regeneration and reuse of these by-products after one complete sorption (adsorption/desorption) cycle resulted in a greater than 70% decrease of their original adsorption capacity (data not shown). The reason for this loss in capacity is not known and is currently being investigated. By comparison, synthetic resins are well-known for their ability to undergo numerous regeneration cycles before replacement. Since cottonseed and soybean hulls can effectively be used only once as a metals adsorbent, this may be seen as a disadvantage. However, there are situations where single-use adsorbents can be utilized.

Wastewater, contaminated with metals and particulate matter, often reduces flow through a resin bed to the extent that backwashing to remove particulates must be carried out at each regeneration cycle. Backwashing is not only time consuming but the backwash must be treated in a separate process stream. In this scenario, the wastewater can be pretreated with single-use adsorbents before exposure to commercial "polishing" resins. The by-product-based adsorbents could capture both metals and particulates, thereby reducing backwashing and extending the useable life of the commercial material.

If hulls are to be used in place of rather than in addition to the resins, then many more tons of hulls will be required for a specific application compared to a ton of resin. This could create a massive waste disposal problem. However, since hulls are also precursors for the production of granular activated carbons, the hulls could be pyrolyzed to produce GACs, and the metals recovered by desorption from the activated carbons.

Pyrolyzed hulls as metal adsorbents

As with non-pyrolyzed hulls, pyrolyzed hulls as GACs must also possess the required adsorption capacity, adsorption efficiency and stability for its intended use. We have compared these properties to several commercial carbons which have been recommended by the manufacturer for adsorption of metals.

Table 6 gives adsorption capacities in equivalents of metal adsorbed per lb of GAC for commercial and by-product-based samples. GACs made from cottonseed and soybean hulls had higher adsorption capacities than the commercial activated carbons when used to remove a mixed suite of metal ions in a laboratory prepared solution. This superior performance is also reflected in the cost to adsorb one equivalent of metal. The commercial GAC samples cost 2-10 times and 3-18 times as much to remove an equivalent of metal as GACs made from cottonseed and soybean hulls, respectively.

Adsorption efficiencies for two of the commercial GACs, namely those made from coconut hulls and lignite coal, were compared to the adsorption efficiencies of GACs made from cottonseed and soybean hulls (Table 7). The percentage of metals removed from an industrial wastewater was superior for all three hull-based GACs compared to the lignite-based sample. In this particular wastewater, removal of metals by the GAC produced from soybean hulls was essentially complete.

Stabilities of commercial and laboratory prepared GACs have not been quantified or compared. Qualitative estimates have indicated that our GACs may be more friable than commercial material in batch applications employing mechanical stirring with a Teflon bar. These perceived differences in particle strength will be quantified and if our GACs are more friable than commercial products, then we must modify our GAC development process to rectify the problem. Improving the physical properties of the by-product-based GACs is a high priority of our ongoing research.

Regeneration studies have not been performed on either our GACs or on the commercial products. Our preliminary studies indicate that our activated carbons can be successfully desorbed with hydrochloric acid but their adsorption capacity after one regeneration cycle remains to be determined.

Conclusions

Our results indicate that a commercial resin (Amberlite® IRC-718) is superior in adsorption capacity, adsorption efficiency and regenerative capacity to washed cottonseed and soybean hulls. However, resin and hull stabilities appear similar. The natural by-product-based adsorbents are considerably less costly than the synthetic resin. In a "real world" situation, effectiveness and cost must be considered simultaneously for a particular application. This report provides data to indicate that non-pyrolyzed cottonseed and soybean hulls possess modest metal adsorbing properties. Because of their relatively low cost, they should be considered as metal adsorbents in applications where the cost of the adsorbent is an overriding factor.

Data acquired thus far show that our granular activated carbons present a very promising picture for the potential conversion of cottonseed and soybean hulls to value-added products. Our GACs show superior adsorption capacities toward metals and show potentially superior market price compared to their commercial counterparts. To remain competitive with commercial GACs, our activated carbons must also be comparable in stability and regeneration properties. These answers await additional research. Some refinement in our pyrolysis and activation procedures will likely be necessary to develop a superior final product. However, development of superior GACs appears to be well within our reach.

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TABLE 1

Resins and Selected By-products: Their Availability and Cost

Adsorbent	Availability (million lbs)	Cost ($/lb)
Cation-exchange resins	92[a]	1.50-20.00[b]
Cottonseed Hulls	3,300[c]	0.03-0.06[d]
Soybean Hulls	9,000[c]	0.09-0.12[d]

[a]1995 estimate from: (Anonymous, 1994d).

[b]Source: see (Anonymous, 1993).

[c]Based on 1993/1994 crop data from: (USDA, 1994).

[d]Estimated bulk cost.

TABLE 2

Commercial and By-product-based GACs: Their Availability and Cost

Adsorbent	Availability (million lbs)	Cost ($/lb)
Commercial GACs	200[a]	1.20-1.50[b]
Cottonseed Hulls	990[c]	1.00[d]
Soybean Hulls	2700[c]	1.00[d]

[a]1995 estimate from: (Anonymous, 1994a).

[b]Source: see (Anonymous, 1994b; 1994c)

[c]Based on 1993/1994 crop data from: (USDA, 1994) and a 30% yield for converting by-products to GACs.

[d]Estimated bulk cost.

TABLE 3

Adsorption Capacities of Selected Adsorbents[a] and Their Cost per Equivalent (Eq) of Metal Adsorbed

Metal Ion or Cost/Eq	IRC-718 (Eq/lb resin)	Cottonseed Hulls (Eq/lb hull)	Soybean Hulls (Eq/lb hull)
Zn(II)	1.39	0.12	0.24
Cu(II)	1.55	0.14	0.28
Ni(II)	1.49	0.11	0.22
$/lb	9.14[b]	0.06[c]	0.12[c]
$/Eq Cu(II)	5.90	0.43	0.43

[a]Modified from: (Marshall and Champagne, 1995).

[b]Source: see (Anonymous, 1993).

[c]Estimated bulk costs.

TABLE 4

Adsorption Efficiencies of Select Adsorbents Based on Percent Metal Removed from Metal Plating Wastewater[a]

Adsorbent	Metal Ion (Percent Adsorbed) Zn(II)	Cu(II)	Ni(II)
Wastewater #1			
IRC-718	98.4	98.8	99.4
Cottonseed Hulls	65.2	80.5	53.4
Soybean Hulls	64.7	83.1	58.7
Wastewater #2			
IRC-718	100	87.2	80.6
Cottonseed Hulls	88.3	74.4	76.7
Soybean Hulls	83.3	82.6	76.8
Wastewater #3			
IRC-718	99.8	100	99.5
Cottonseed Hulls	89.4	91.2	89.4
Soybean Hulls	89.8	99.8	87.8

[a]Source: (Marshall and Champagne, 1995).

TABLE 5

Degree of Stability[a] (Percent Solids Retained) of Selected Adsorbents

Adsorbent	Solids Retained (%)
IRC-718	93.6
Cottonseed Hulls	99.4
Soybean Hulls	98.3
Stabilized Rice Bran	76.1
Non-Stabilized Rice Bran	80.2

[a]Batch adsorption conditions: samples mechanically stirred (Teflon bar) in 0.1 N acetate buffer, pH 4.7 at 25°C for 2 hr.

TABLE 6

Adsorption Capacities[a] of Select GACs Based on Their Cost Per Equivalent of Metal Adsorbed

GAC Precursor	Adsorption Capacity (Eq/lb)	Cost/lb ($/lb)	Cost/Eq of Metal Adsorbed ($/Eq)
Extruded Peat[b]	0.24	1.38	5.75
Bituminous Coal[b]	0.22	1.38	6.27
Coconut Hulls[b]	0.20	1.50	7.50
Lignite Coal[b]	0.04	1.22	30.50
Cottonseed Hulls	0.34	1.00[c]	2.94
Soybean Hulls	0.58	1.00[c]	1.72

[a]One gram of GAC was added to 100 mL of a solution containing 2.5 mM each of cadmium, copper, lead, nickel and zinc ions at pH 5.0.

[b]Commercial GACs.

[c]Estimated Bulk Cost.

TABLE 7

Adsorption Efficiencies[a] of Select GACs Based on Their Percent Metal Removal from Metal Plating Wastewater

GAC Precursor	Metal Ion (Percent Adsorbed) Zn(II)	Cu(II)	Ni(II)
Coconut Hulls[b]	100	99.8	97.6
Lignite Coal[b]	40.5	94.3	24.3
Cottonseed Hulls	100	98.4	94.0
Soybean Hulls	100	99.9	99.5

[a]One gram of GAC was added to 100 mL of metal plating wastewater. The mixture was stirred for 2 hr at 23°C and pH 5.0.

[b]Commercial GACs.

SALMONELLA & HACCP FOR THE FEED INDUSTRY

by

Robert E. Broyles
Director Regulatory, Quality & Safety
Purina Mills
St.Louis, Missouri

The Food & Drug Administration (FDA) has expressed concerns relative to Salmonella in feed relative to our industry for many years. Some of the highlights of past interaction between FDA and our industry in resent times would include;

- In 1987 American Feed Industry's Task Force (AFIA) on Salmonella in feeds met in Washington DC and established strategy for legislation and agreed to update AFIA's Guidelines for Sanitation Practices by March 1988.

- AFIA's Oakly Ray wrote Dr. Guest FDA September 24, 1990, and expressed great concern about CVM's proposal to initiate a major program to reduce the salmonella content of feed to zero.

- Key CVM representatives since have continued to articulate agency policy in presentations to many agricultural interested groups. The thrust of these FDA stated concerns included the notion that salmonella contamination in feed may adversely affect animal and human health and therefore must be removed from feed and feed ingredients. According to these presentations to accomplish 0 salmonella the industry must identify critical control points employed in a Hazard Analysis Critical Control Program.

- Because of continuing and accelerating CVM activity relative to salmonella in feed, AFIA's Board of Directors approved an eight point program at their May 1993 meeting entitled; "Recommendations of the Salmonella Task Force". AFIA then established a new Microbiological Control Task Force with the charge to develop a HACCP-type program for the feed industry. It was requested that the program be developed by May of 1994. There was and still is complete recognition and understanding that zero salmonella in feed is not obtainable.

(see attached recommendations)

The new task force met January, 1994 and developed a Mission Statement, objectives, and action plans.

(see Attached 'Mission Statement' and action plans)

RECOMMENDATIONS OF THE SALMONELLA TASK FORCE

1. AFIA should distribute the AFIA-produced "Recommended Salmonella Control Guidelines for Processors of Livestock and Poultry Feeds" to AFIA members, state/regional feed manufacturers and producers groups with a letter from the Salmonella Task Force strongly recommending use of the guidelines and announcing the development of a HACCP-type program for the feed industry.

2. AFIA should form a Microbiological Control Task Force (MCTF) to develop in suitable format a Hazard Analysis Critical Control Point (HACCP)-type program based on the AFIA's "Recommended Salmonella Control Guidelines for Processors of Livestock and Poultry Feeds." The task force should seek input from U. S. Animal Health Assn. (USAHA) members and producer groups. In creating the task force, expertise should be drawn from the AFIA Feed Control, Manufacturing and Purchasing Committees; the Quality Assurance Committee of the Nutrition Council; and Laboratory Committee of the Ingredient Suppliers Council.

3. The USAHA's Feed Safety Committee's Feed and Feed Ingredients Subcommittee should review the various national HACCP-type programs for uniformity and consistency between and among ingredient suppliers.

4. Any HACCP-type program developed should be limited to those true critical control points.

5. The Salmonella Task Force should be continued during the HACCP-type program development. This will assist in providing input to the MCTF and interfacing with the USAHA's Feed Safety Committee's working subcommittees.

6. AFIA should commit up to $10,000 for the use of the MCTF in the development of the HACCP-type program. Recovery of costs to be from the sale of the program to members and non-members. Each member firm will be provided one free copy of the program. Commitment of the funds is dependent on the acceptance of the principles embodied in recommendations 2-6 by the USAHA Feed Safety Committee in Fall of this year at the USAHA Annual Meeting.

7. For valid scientific reasons (lack of validity in retroactive review of microbiological data, uncertainty of the quality of data or analytical methodologies, etc.), AFIA should recommend members use extreme caution and discretion in the release to USAHA or FDA of any results from microbiological sampling and analysis.

8. AFIA should continue to promote and recommend feed manufacturers purchase ingredients from suppliers with proven, recognized quality assurance and/or microbiological contamination reduction and education programs.

AMERICAN FEED INDUSTRY ASSOCIATION

MICROBIOLOGICAL CONTROL TASK FORCE

MISSION STATEMENT

To identify, develop and propose suitable HACCP-type microbiological principles applicable to the feed industry considering the upstream and downstream needs and effects in the framework of animal production.

OBJECTIVES

1. To focus/coordinate with other ingredient, producer and feed groups, e.g. NCA, NG&FA, NBC, NPPC, NMPF, APPI, NOPA, etc.

2. To seek further expert information on:

   a. Analysis technology.
   b. Threshold limits of Salmonella in public health.
   c. Threshold limits of Salmonella in veterinary public health by species.
   d. HACCP principles for the feed industry.
   e. Breadth and scope of the feed industry.
   f. Status of food additives approved for microbiological control in feed.
   g. Status of research on Salmonella in feeds.

3. To interface with FDA on:

   a. Definition of "zero tolerance" of Salmonella in feeds.
   b. Breadth and scope of any required HACCP plan for animal production, i. e. from "farm to fork."
   c. Comment on advance notice of proposed rulemaking regarding HACCP programs.

4. To inform the AFIA membership and make available contamination and Salmonella control publications.

5. To identify, develop and propose suitable HACCP-type microbiological principles

6. To review and draw conclusions on the impact of any principles proposed.

7. To propose a plan to the AFIA Board of Directors.

ACTION PLANS

1. Letter to membership, producers, ingredient groups and others with AFIA Salmonella Control Guidelines and contamination brochure recommendations.

   Date: February 1, 1994
   By: Sellers

2. Begin coordination with ingredient groups, producer groups, other feed-related groups and FDA.

   Date: Meeting in mid-March
   By: Sellers to draft letter and coordinate dates

3. Begin collecting expert information on:

   a. Analysis technology--Shermer
   b. Public health limits of Salmonella--Sellers
   c. Veterinary public health limits of Salmonella--Sellers to contact Dr. Gavin Meerdink, USDA/APHIS/NVMDL
   d. HACCP principles for the feed industry--Werner
   e. Breadth and scope of the feed industry--Sellers will contact the AFIA Economic & Market Research Committee
   f. Microbiological control feed additives--at FDA meeting
   g. Status of research on Salmonella in feeds--Harriman to contact Drs. Bailey and Cox at USDA/ARS, Athens, GA

AFIA's task force since has carried through on its stated mission, objectives, and action plans. The task force met with upstream and down stream groups which included representatives form virtually all feed suppliers, animal producer groups, and animal product processing groups. The task force met with FDA's CVM and with US Animal Health Association's (USAHA) committee which has made recommendations to FDA relative to salmonella in feed issues. The task force surveyed groups that are upstream and down stream from feed interest to determine their present technology and needs relative to Microbiological controls.

From all of the above stated contacts and inputs, the committee has developed a Microbiological HACCP-type program for the feed industry (copy attached) which is consistent with our Mission Statement and findings from our investigations.

The committee is now requesting AFIA's board approval of the recommended feed industry HACCP-type program. Following approval, the program is to be distributed to AFIA member companies, the Association of American Control Officials, and state feed and grain associations. The HACCP-type program is a voluntary program to be employed for microbiogical control in the manufacture of animal livestock feed.

AFIA (HACCP-TYPE) GUIDELINE
FOR FEED MANUFACTURING FACILITY
SALMONELLA CONTROL

- **TRAINING:**

- Employees are to be trained in their areas of responsibility to identify potential contamination issues of their activities.

- **Supplier Selection:**

- Ingredient suppliers should certify that their manufacturing procedures and controls are conducted in accordance with CGMP's appropriate for their business. Ingredient suppliers should be encouraged to develop sanitation and process standards for their specific ingredient. Voluntary compliance with the industry standard should be encouraged through appropriate trade associations, and through feed manufacturers demanding development and compliance with such standards if they are to be an approved feed ingredient supplier to the feed manufacturer.

- **Ingredient Receiving:**

- Each ingredient should have a receiving specification sheet and be inspected for compliance with the specifications established for the ingredient prior to unloading. Microbiological issues would include assurance that the ingredient is from an approved certified supplier. The initial discharge from a truck or rail car should be caught and examined for visual contaminates such a foreign material, excessive moisture, or unsanitary conditions.

- The transportation vehicle should be in good sanitation condition visually, and the feed sample should appear to be free from visual contamination, excessive moisture, and look as described in the ingredients written specification.

- Incoming bag ingredients checked for visual exposure to moisture or contamination.

- A written sanitation program is be in effect in the unloading area and good sanitation practiced. Unloading pits are to be free from excessive moisture and other feed material. Area should be reasonably free from birds and rodents. Pits should be covered when not in use.

- Reprocessed material from any source should not be used if it has been subjected to high moisture conditions, or held under unsanitary conditions.

- **Housekeeping & Sanitation:**

- A written housekeeping program should be in effect for all areas of the manufacturing facility (including grounds). The housekeeping program shall include what is to be done, when each item is to be done, and designate responsible employee. Documentation of program compliance should be maintained at the facility.

- A written pesticide and rodenticide program should be in effect for all areas of the manufacturing facility (including grounds). The pesticide program shall include what is to be done, when each item is to be done, and designate responsibility, In the event that some or all pesticide activities are conducted by an outside contractor, the contractor is to provide a written record for those issues of responsibility. Documentation of program compliance should be maintained at the facility.

- Moisture within the manufacturing facility should be kept to a minimum, especially in areas that would supply air to coolers, or come in close contact with feed storage bins, legs, or other feed conveyances.

- **Pelleting Systems**

- Inside of pellet mill doors shall be cleaned before shut down for over an 8 hour period and left open to dry.

- Pellet mill temperatures should be maintained as high as possible, but it is recognized that such temperatures must be consistent with maintaining compliance with physical finished product specifications, and nutrient content.

- Moist cleanings from the pellet mills must not go to reprocessed material.

- Coolers maintained in a reasonably clean condition.

- **Bulk load-out**

- Be reasonably free of birds

- All trucks examined for cleanliness prior to loading

- After period of shut down (over week end), examine scale for dead birds or fecal material prior to start up

- Plug any dead spouts on turn heads to prevent feed accumulation

- **Packaging**

- Packaging should be inspected for visual contamination prior to use

- Watch molasses buildup in scales

- Do not exceed finished product moisture standards with packaged product

- **Records**

- A record is to be maintained of these activities for a minimum period one year.

SPECIAL REPORT

FDA survey determines salmonella contamination

First comprehensive study of animal and vegetable protein meal finds both carry salmonella, including *Salmonella enteritidis*.

By DANIEL G. McCHESNEY, GILBERT KAPLAN and PATSY GARDNER

In September 1990, the Food & Drug Administration's Center for Veterinary Medicine (CVM) announced a goal of zero salmonella contamination in animal feed ingredients and finished feed. One of the recommendations of CVM's Salmonella Working Group was to establish an FDA monitoring program for salmonella in feed and feed ingredients. Toward this end, FDA conducted a survey in 1993 of processors manufacturing either animal or vegetable protein products used in animal feeds in order to collect information on the prevalence of salmonella. FDA will use this information in establishing a baseline of salmonella contamination.

Methods

FDA investigators aseptically collected samples of products described by the manufacturer as meal from 100 animal protein processors and 68 vegetable protein processors. Manufacturers were selected from FDA's Official Establishment Inventory, from common business reference material and other lists available in public documents.

In general, we attempted to select two manufacturers in each state and avoid sites within a state belonging to the same manufacturer.

From the original list of 100 animal and 68 vegetable processing plants, investigators were able to collect samples from 78 animal and 46 vegetable protein processors. Some of the firms on the original lists did not manufacture meal, were brokers, dealers or offices, or were doing business under another name on the list.

For the animal processor "washout" firms, CVM provided substitute firms. No substitute vegetable firms could be given, because the original list contained all firms that could be identified.

While at the plants, the investigator aseptically collected 30 subsamples per sample of feed ingredients that the processor had identified as meal products. Each subsample consisted of approximately 100-200 g of meal collected in sterile, whirl-pack bags from bulk or bagged products. In some instances, especially with animal protein processors, this resulted in multiple samples being collected because more than one meal product was on hand. No more than two meal varieties per plant were sampled.

All samples were collected at the "loadout point." All subsamples comprising a sample were sent to a FDA laboratory for compositing and analysis.

The laboratory prepared two composites of the 30 subsamples consisting of subsamples 1-15 and 16-30. Each composite was analyzed by the method stated in the 7th Edition of the *Bacteriological Analytical Manual* (BAM), Chapter 5. Results were reported to CVM as positive or negative.

A sample was considered positive if either of the composites were positive. No quantitation or speciation was requested in the assignment. However, approximately 23% of the samples were either serogrouped or serotyped by FDA laboratories. The method(s) used for serogrouping and serotyping are stated in the 7th Edition of the BAM.

Results, discussion

The results are from 151 individual samples with each sample consisting of 30 subsamples. Thus, the findings represent the results of 4,530 individual samples (3,030 subsamples of animal protein a 1,500 subsamples of vegetable protein) approximately 100 g each.

One hundred and one samples of anim protein products and 50 samples of ve etable protein products were analyzed

Salmonella was detected in 56.4% the animal protein samples and 36% the vegetable protein products (Table

The results in Table 2 use the sar sample data as used for Table 1, but rep the results based on individual proce sors. Thus, while 62% of the animal pr tein processors had salmonella-positi product, only 56.4% of the individu samples were positive. This indicates th multiple products were sampled at son animal protein processors and that in few cases the results for the produc sampled were different.

With regard to vegetable protein pr cessors, 37% of the processors and 36 of the samples were positive for salm nella. The 1% difference is the result one processor being visited twice durin the course of the survey and in both i stances having product test positive f salmonella.

The sampling plan that was used had th theoretical possibility of detecting or organism in 278 g of product. Anothe way of stating this is that, if 5% of th sample units in a lot contain salmonell there was a 21% chance that the samplin plan would not detect salmonella.

However, if 10% of the sample units i a lot contain salmonella, there was only 4% chance that the sampling plan woul not detect salmonella and at 20%, les than a 1% chance that salmonella woul not be detected.

FDA chose this sampling plan to begi establishing a baseline of salmonell prevalence data. If a less stringent sam pling plan were used, it would have bee difficult to detect salmonella at low preva lence levels.

On a positive note, the stringency of th sampling plan means that all plants test ing negative had, on that day and for th specific product, a greater than 99% chanc of having product that had less than 20% of the analytical units positive for salmo nella.

The survey was not designed to quanti tate the number of salmonella present vi the Most Probable Number (MPN), no were the individual subsamples compris ing a positive composite analyzed indi vidually to provide a semiquantitativ estimate. However, based on the theoreti

TABLES

1. Salmonella isolates from animal, vegetable protein products

	Total samples	Positive samples	Percent positive
Animal	101	57	56.4
Vegetable	50	18	36.0
Total	151	75	49.7

Each sample consisted of 30 subsamples. The 30 subsamples were divided into two composites of 15 subsamples each for analysis. A sample was considered positive if either of the composites were positive. In some cases, especially with animal protein products multiple samples were collected because more than one meal product was on hand.

2. Salmonella isolates from animal, vegetable protein processors

Plant	Total plants	Positive plants	% Positive plants
Animal	78	48	62*
Vegetable	46	17	37
Total	124	65	

*% Positive plants are significantly different at p<0.01.

3. Sample results for composites

Plant	Total samples	Total positive samples	Number positive samples with one positive composite	Number of plants with one positive composite
Animal	101	57	16	15
Vegetable	50	18	9	9

4. Number of salmonella isolates by meal type from animal protein products

Type meal	Total samples	Positive samples
Animal protein byproducts	4	3
Beef/bone meal	1	1
Blood	6	3
Bone meal	1	1
Dried plasma	1	0
Feather meal	14	5
Feather/blood	1	0
Fish	4	3
Meat/bone meal	42	27
Meat meal	3	2
Meat/bone/poultry	1	1
Pork blood	2	0
Poultry byproduct	4	2
Poultry	17	9
Subtotal	101	57

■ *Daniel G. McChesney, Gilbert Kaplan and Patsy Gardner are with the Office of Surveillance & Compliance, CVM, Rockville, Md.*

TABLES

5. Number of salmonella isolates by meal type from vegetable protein products

Type meal	Total samples	Positive samples
Corn germ meal	1	0
Cottonseed meal	8	3
Linseed meal	1	0
Peanut meal	2	2
Rapeseed meal	1	1
Safflower meal	2	2
Soybean meal	33	8
Sunflower meal	2	2
Subtotal	50	18
Grand Total	151	75

6. Salmonella serogroup and serotype by animal protein product

Type meat	Serogroups	Serotypes
	C1, E3, E4, K	*senftenberg, cerro*
Animal protein byproducts		
Beef/bone meal	NG (1 positive)	NS
Blood	B, C1	*brandenburg, livingstone*
Bone meal	B	*brandenburg, schwarzengrund*
Dried plasma	(no positives)	
Feather meal	B, C1, poly Group D	NS
Feather/blood	(no positives)	
Fish	poly Group A	NS
Meat/bone meal	B, C1, E1, E2, E4, R, poly Group C, poly Group D	*binza, uganda, johannesburg, tennessee*
Meat meal	C1	*tennessee*
Meat/bone/poultry	C1	*montevideo*
Pork blood	(no positives)	
Poultry byproduct	B, C1, E2, K	*california, agona montevideo, cerro, newhaw*
Poultry	B, C1, E2, R, poly Group B, poly Group D	*montevideo, newhaw, johannesburg*

NS= not serotyped

7. Salmonella serogroup and serotype by vegetable protein type

Type meal	Serogroup	Serotype
Corn germ meal	(no positives)	
Cottonseed meal	C1, E4	NS
Linseed meal	(no positives)	
Peanut meal	(2 positives) NG	NS
Rapeseed meal	C1	*tennessee*
Safflower meal	E2	NS
Soybean meal	D1, E1	*enteritidis, cubana, senftenberg, montevideo*
Sunflower meal	(2 positives) NG	NS

NS= not serotyped

included in Table 6.

Of particular note was the isolation of *Salmonella enteritidis* from soybean meal. To our knowledge, *S. enteritidis* has not been previously reported in a vegetable meal in the U.S. The Animal & Plant Health Inspection Service of the U.S. Department of Agriculture reported the isolation of *S. enteritidis* from meat and bone meal collected at a duck growing facility in 1992 (*S. enteritidis* Task Force Status Report, Sept. 28, 1992). The National Veterinary Services Laboratory (NVSL) has reported isolating *S. enteritidis* from feed in 1991, 1992 and 1993, but not prior to 1991. The 1994 data from NVSL are not yet available.

Additionally, *S. enteritidis* has been isolated from a Swedish feed mill (Gunnarsson, et. al., Acta vet. scand, 1991, 32, 261-277) and vegetable meal in Europe (personal communication, Dr. Richardson).

The reporting of *S. enteritidis* from animal feedingstuffs in still uncommon, but seems to be increasing. Whether the increase in reporting is the result of increased awareness resulting in increased sampling of these products or an indication of a growing niche for *S. enteritidis* cannot be determined from these data.

Summary

The data indicate that salmonella occurs in both animal and vegetable protein samples. The information on samples in which only one composite was positive suggests on a qualitative basis that the salmonella load in vegetable meal products may be slightly less than in animal meal products. We cannot determine whether the small difference is of practical importance when formulating feed.

Therefore, it is our view that the exclusion of one of these products in favor of the other is not a valid approach to ensuring a salmonella-negative feed.

We recommend that purchase contracts for meal products incorporate a salmonella-negative specification. Toward this, the Feed Safety Committee of the U.S. Animal Health Assn. (USAHA) recently accepted the report of the microbiology subcommittee, in which the subcommittee recommended 10 samples (subsamples) for routine monitoring of salmonella contamination. For products with a reduced risk, the subcommittee recommended five samples (subsamples). However, products falling into the reduced risk category were not identified.

These data are the beginning of the establishment of a baseline for the various segments of the feed industry. We have shared these with the USAHA.

The Feed Safety Committee of USAHA at the 1994 annual meeting recommended that three surveys be undertaken to add to and expand the data base for the baseline. The committee recommended that one survey be conducted of the feed ingredient industry, another conducted at feed mills to include finished feeds and their ingredients and a third of transportation vehicles. USAHA would develop an operational protocol for the conduct of the baseline studies and industry would voluntarily pull and analyze samples. The results are to be submitted to a university for coding and analysis of the data.

FDA will continue surveys under its Feed Contaminants Program. These surveys will be in addition to those recommended by USAHA and are intended to bridge the information gap while the USAHA surveys become established. ■

e limit of the sampling plan and the mber of samples in which only a single mposite was positive (Table 3), we can ovide a qualitative assessment of the ative contamination levels in animal r vegetable protein products.

here were a total of 75 positive samples, which 25 samples had only a single mposite positive. Compositing assumes a single positive subsample will re- in the composite testing positive.

herefore, a negative composite sug- ts that none of the 15 subsamples are itive, while a positive composite sug- s that one or more of the 15 subsamples positive for salmonella. Thus, having y one of the two composites positive lies that 15 or more of the subsamples the 30 collected were negative for monella and points to a lesser degree of monella contamination. The probabil- of selecting 15 negative subsamples a single composite in a sample in ch two of the 30 subsamples are posi- is 24%. When four of the 30 samples are positive, the probability is 8%; and when eight subsamples are itive, the probability is 0.10%.

ased on the sampling plan used and difference in the number of positives ingle composites, and the number of cessors with single composite posi- s, vegetable products and processors y have a slightly lower level of salmo- a contamination than animal protein ducts and processors.

of the meal and, thus, a definitive statement about the likelihood of salmonella in these meal types cannot be made.

The assignment did not require the analyzing laboratory to either serogroup or serotype positive isolates. However, several laboratories on their own initiative either serogrouped or serotyped the isolates. Those isolates that were serogrouped or serotyped represent 23.2% (35/151) of the isolates. Tables 6 and 7 present the results. In those instances in which only the serotypes were reported, the corresponding serogroup was identified and

CURRENT DEVELOPMENT OF RICE BRAN OIL

by

Frank T. Orthoefer
Vice President, Research and Development
Riceland Foods, Inc.
709 E. 22nd St.
Stuttgart, Arkansas 72160, U.S.A.

Several new facilities are under construction or are actively producing rice bran oil for edible applications. The major process considerations for producing a high quality refined oil are stabilization of the bran immediately after milling, temperature of extraction (if hexane is used) and refining method. A finished rice oil may be produced that has the characteristics and applications similar to peanut oil with nutritional benefits associated only with rice oil.

Introduction:

The initial work on rice oil in the U.S. began about 50 years ago to enhance the value of rice bran, a by-product of rice milling. Recent nutritional investigations have shown rice oil to have significant positive effects on lowering serum lipids. This led to an import opportunity for rice oil to the U.S. Now, rice oil is being exported to user countries, particularly Japan and Korea. It is now being evaluated as an oil that behaves similarly to peanut oil in frying evaluations.

Rice Bran Versus Oat Bran:

American and other researchers discovered a few years ago that rice bran when incorporated into the diet could reduce serum cholesterol similar to oat bran (Hegsted et. al., 1990, Gerhardt and Gallo, 1989). The ready-to-eat breakfast cereal producers rushed to get the bran into their products. Similar to oat bran, rice bran as a food ingredient suffered the same fate as oat bran when studies showed that normo-cholesterolemic individuals showed no or limited response to oat bran.

Compared to oat bran, rice bran is low in soluble fiber, the constituent of oat bran believed responsible for cholesterol reduction (Table 1). Several components of rice bran were believed to affect serum cholesterol levels. These are the sterols, hemicellulose and unsaturated oils (Table 2). Defatted rice bran was not found to be as active in lowering serum cholesterol as full fat rice bran. The oil fraction was obviously implicated as the active constituent (Kahlon, et. al. 1992) (Table 3).

Rice Bran as a Source of Oil:

There is approximately 500 million metric tons of rice produced annually or approximately 1/4 of all the cereal grains produced. The bran constitutes about 10% of rough rice and contains almost all the oil and the majority of the protein, ash, vitamins and fiber present in rice (Table 4). The oil content of clean rice bran (18 to 20%) is similar to that of other oilseeds such as soybeans and cottonseeds. A potential of about three million metric tons of rice oil exists world wide. This compares roughly to cottonseed oil production.

Only 450,000 metric tons of crude rice oil are currently produced. Japan has an annual production of about 100,000 metric tons of edible rice oil. The potential in the United States is about 82,000 metric tons. A practical estimate of the potential U.S. production is about one half the total estimate because of the dispersed production of the bran among several rice millers most having insufficient supplies of bran to justify oil extraction. Consequently, several rice millers have joined

with entrepreneurial partners to produce rice bran oil. Only Riceland Foods, Inc. and a joint venture partner, RITO, have constructed extraction facilities and are currently producing rice bran oil at its Stuttgart, Arkansas, USA facility.

Production of Rice Bran Oil:

Rice bran, while intact on the whole kernel, is stable. Once the bran is milled from the grain, the oil is rapidly hydrolyzed to free fatty acids and glycerol by a lipase enzyme (Figure 1). Development of 4 to 5% free fatty acids per day occurs (Saunders, 1986). Refining losses are generally in the 18 to 22% range which may be several times the free fatty acid content. Oil in the intact bran contains about 2 to 4% free fatty acid.

The bran may be stabilized by lipase inactivation through heat treatment or pH manipulation. Extrusion cooking was developed by the Western Regional Research Laboratory, Albany, California, as a cost effective stabilization technique (Sayre et. al., 1982).

Conversion of the bran to a pellet or collett form improves extraction efficiency when using hexane as the extraction solvent. Once stabilized and pelleted, the bran may be stored before extraction without an increase in free fatty acid content. Extraction times and temperature have been shown to affect yields, wax content, and gums in the crude oil (Orthoefer, 1994). Analysis of a typical crude rice oil is shown in Table 5. The neutral lipid and free fatty acid content of a properly stabilized and extracted crude rice oil are 90% and 2 to 4%, respectively.

Both alkali and physical refining methods have been applied to rice bran oil. The high free fatty acid, wax, and unsaponifiable content often lead to high refining losses. Wax removal and winterization are particularly difficult. The crude oil may also be used as a source of oryzanol, phospholipids, and edible waxes (Table 6). The specifications for a fully refined, bleached and deodorized U.S. produced rice bran oil is shown in Table 7.

The fatty acid composition of rice bran oil is most similar to groundnut (peanut) oil (Table 8). The most notable difference is in the long chain saturated fatty acid content (C20:0 and 22:0). Similar to peanut oil, rice oil is most suited to general cooking and frying applications.

Rice Bran Oil Nutrition:

The hypocholesterolemic activity of rice bran oil is

concentrated in the unsaponifiable fraction (Table 9). The serum cholesterol reduction occurs primarily in the LDL cholesterol. Increased fecal excretion of bile acids and neutral sterols occurs when rice bran oil is fed to rats (Sharma and Rukmini, 1986). Oryzanol, a major component of rice unsaponifiables, was found to contribute to the hypocholesterolemic activity of rice oil in hampsters (Nicolosi, et. al. 1992). Tocotrienols, also present in rice oil, have been reported to reduce serum cholesterol levels (Nicolosi, 1990). The tocotrienol effect has been difficult to validate.

The refining method has a major effect on the oryzanol content of refined rice bran oil. With alkali refining, most of the oryzanol is removed (Figure 2). With physical or steam refining the oryzanol remains in the oil.

Rice Bran Oil as a Frying Oil:

Rice bran oil is utilized in Japan primarily as a frying oil. Yuki (1988) compared the stability of rice bran oil to other vegetable oils in a model system simulating deep frying conditions. Rice oil showed equivalent or better oxidative stability compared to soybean, canola, corn, cottonseed, and safflower oils. A lower change in carbonyl content and a smaller increase in viscosity was also observed for rice bran oil.

For general purpose frying applications for meat and vegetable products, rice oil was compared to peanut oil and cottonseed oil in model frying evaluations (Table 10). Rice oil was equivalent to or better than peanut oil through the test period and better than cottonseed oils. Blends of rice oil with soybean oil tended to reduce the rate of increase of total polar material (TPM) depending on the content of rice oil in the blend (Table 11).

Rice oil for frying of potato chips was evaluated for shelf life using the Schaal oven test (Gould, 1976) (Table 12). The potato chips prepared with rice oil exhibited flavor and odor stability at elevated storage temperatures between that of peanut oil and cottonseed oil.

Conclusions:

Significant quantities of rice oil are being produced from new facilities in the USA. The oil is similar to peanut (groundnut) oil in composition and functional characteristics but at significant cost savings with the added advantage of nutritional benefits.

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Table 1. Typical Composition of Rice Bran

Protein	15%
Oil	18%
Ash	7%
Carbohydrates	50%
Fiber:	
Crude	7%
Total Dietary	28%
Soluble Fiber	2.4
Insoluble Fiber	25.6

Table 2. Factors in Rice Bran Which May Contribute to Lowering Cholesterol.

* Tocotrienols
* Oryzanols
* B-Sitosterol
* Hemicelluloses
* B-Glucan
* Oil Unsaturation
* Protein

Table 3. Effect of Rice & Oat Brans on Serum Cholesterol in Hamsters (Kahlon, et. al., 1992).

Bran in Diet (%)*	Serum Cholesterol (mg/dl)
Cellulose (10%)	395
Rice bran (47.8%)	270
Defatted rice bran (24.7%)	347
Parboiled rice bran (31.8%)	297
Defatted parboiled rice bran (19.6%)	377
Oat bran (53.7%)	289

* plus 0.5% cholesterol

Table 4. Relative Proportion of Major Rice Caryopsis Components

Component	%
Hull	20
Bran & Germ	10
Starchy Endosperm	70

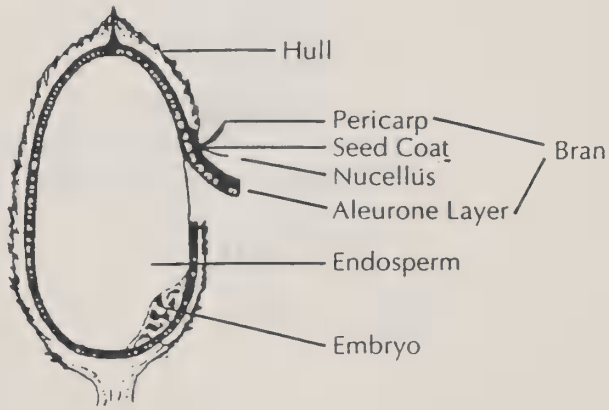


Table 5. Crude Rice Bran Oil Composition

Saponifiable Lipids	90-96%
Neutral Lipids	88-89%
Triglycerides	83-86%
Diglycerides	3 - 4%
Monoglycerides	6 - 7%
Free Fatty Acids	2 - 4%
Waxes	3 - 4%
Glycolipids	6 - 7%
Phospholipids	4 - 5%
Unsaponifiable Lipids	4.2%
Phytosterols	43%
Sterolesters	10%
Triterpene Alcohols	28%
Hydrocarbons	18%
Tocopherols	1%

Table 6. Products from Crude Rice Bran Oil

* Edible Rice Bran Oil
* Free Fatty Acids
* Glycerol
* Oryzanol
* Phospholipids
* Wax
* Sterols, Triterpenes & Tocopherols

Table 7. RICE BRAN OIL: Product Specifications

COMPOSITION: Refined, Bleached & Deodorized Rice Bran Oil

TYPICAL ANALYSIS:

Iodine Value (wijs)	99 - 108
Peroxide Value (meq/kg)	1.0 max
Moisture (%)	0.05 max
Color (5 1/4" Lovibond red)	5.0 max
Free Fatty Acid (% as oleic)	0.05 max
Flavor/Odor	7 min
Chlorophyll (ppb)	75 max
Saponification Value	180 - 190
Unsaponifiable Matter	3 - 5
Smoke Point	213 C
Refractive Index	1.470-1.473
Specific Gravity	0.916
AOM (hrs)	17.5

Table 8. Chemical Composition of Rice Bran Oil (RBO) & Ground Nut Oil (GNO).

	RBO	GNO
1. Physicochemical parameters		
Acid Value	1.2	1.2
Iodine Value	100.0	100.2
Sap Value	211.8	206.2
Unsap. matter	4.2	0.4
2. Fatty acid composition (%)		
C14:0	0.6	----
C16:0	21.5	14.4
C18:0	2.9	3.1
C18:1	38.4	42.6
C18:2	34.4	35.9
C18:3	2.2	----
C20:0	----	2.7
C22:0	----	1.0

Table 9. Hypocholesterolemic Activity of Unsaponifiable Matter of Rice Bran Oil in Rats (Sharma and Rukmini, 1987).

Diet*	Serum Cholesterol (mg/dl)		
	Total	HDL	LDL + VLDL
Control (peanut oil) (10%)	374	43	331
Rice bran oil (10%)	288	48	240
Control + 0.2% unsaponifiables	387	48	339
Control + 0.4% unsaponifiables	243	48	195

* 1% cholesterol added

Table 10. Frying evaluation of rice oil (15 day results).

Oil type	FFA	FOS	Days to max. Lovibond Yellow	Lovibond Red	TPM
Rice oil (w/o additives)	3.91	3.74	6	28.0	31.9
Rice oil (wi additives)	5.62	3.46	7	49.6	34.6
Peanut oil (wi additives)	6.87	3.92	8	21.2	35.5
Cottonseed oil (wi additives)	7.22	4.07	7	28.8	37.2

- 40 lb. (18.2 Kg) gas fryers
- frying temperature 350 degrees F (177 degrees C)
- hourly rotation: breaded chicken, fish, onion rings, french fries
- additives: 5 ppm dimethyl polysiloxane antifoam, 200 ppm TBHQ
- FFA = free fatty acids
  FOS = food oil sensor
  TPM = total polar material

Table 11. Frying results using blends of rice oil and soybean oil (see table 10 for trial conditions).

Oil	Total polar material	
	10 days	15 days
Rice oil	21.12	32.78
Peanut oil	21.07	35.53
50/50 Rice oil/Soybean oil	24.11	35.80
25/75 Rice oil/Soybean oil	23.25	40.42

Table 12. Days at 145 degrees F (62.8 C) before rancid odor detected.

Oil type	Days to detect rancid odor
Rice oil (w/o additives)	20
(wi additives)	25
Peanut oil (w/o additives)	14
Cottonseed oil (wi additives)	31

Figure 1.

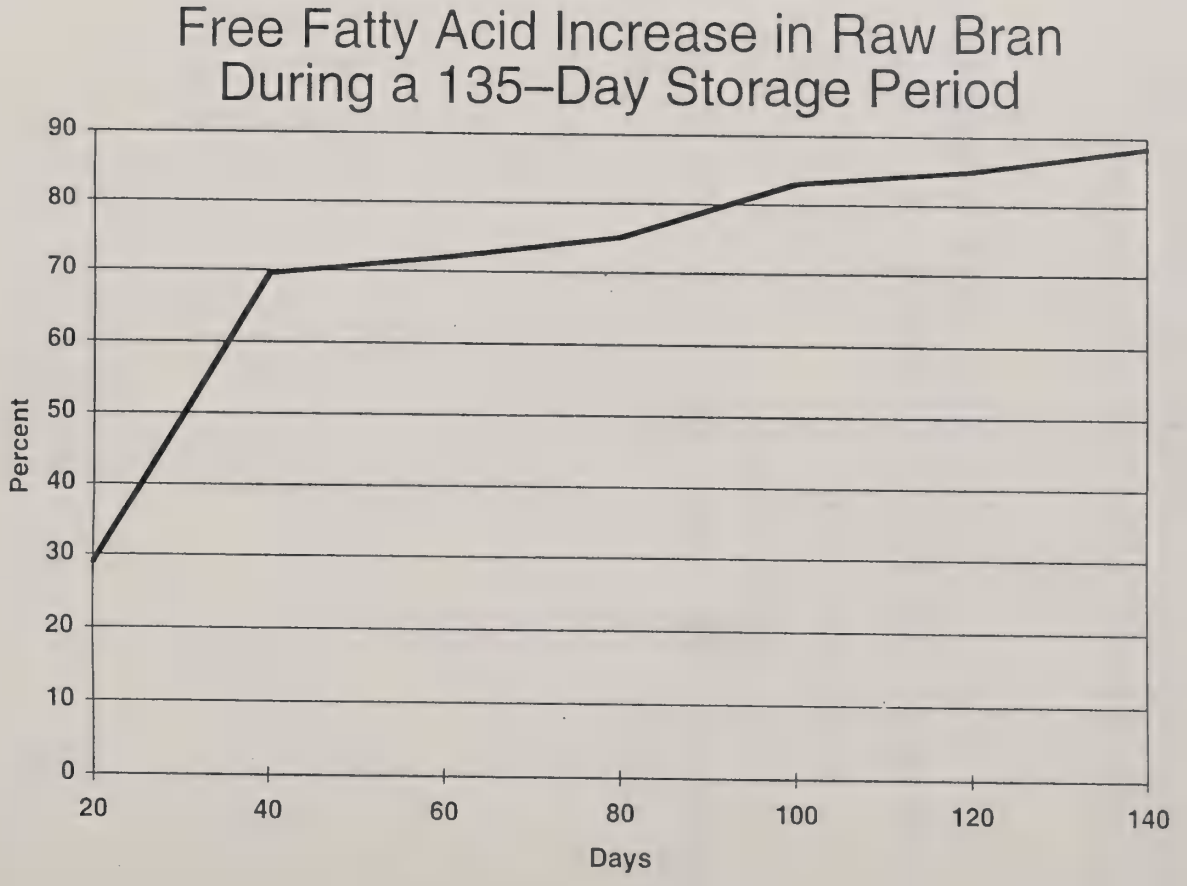
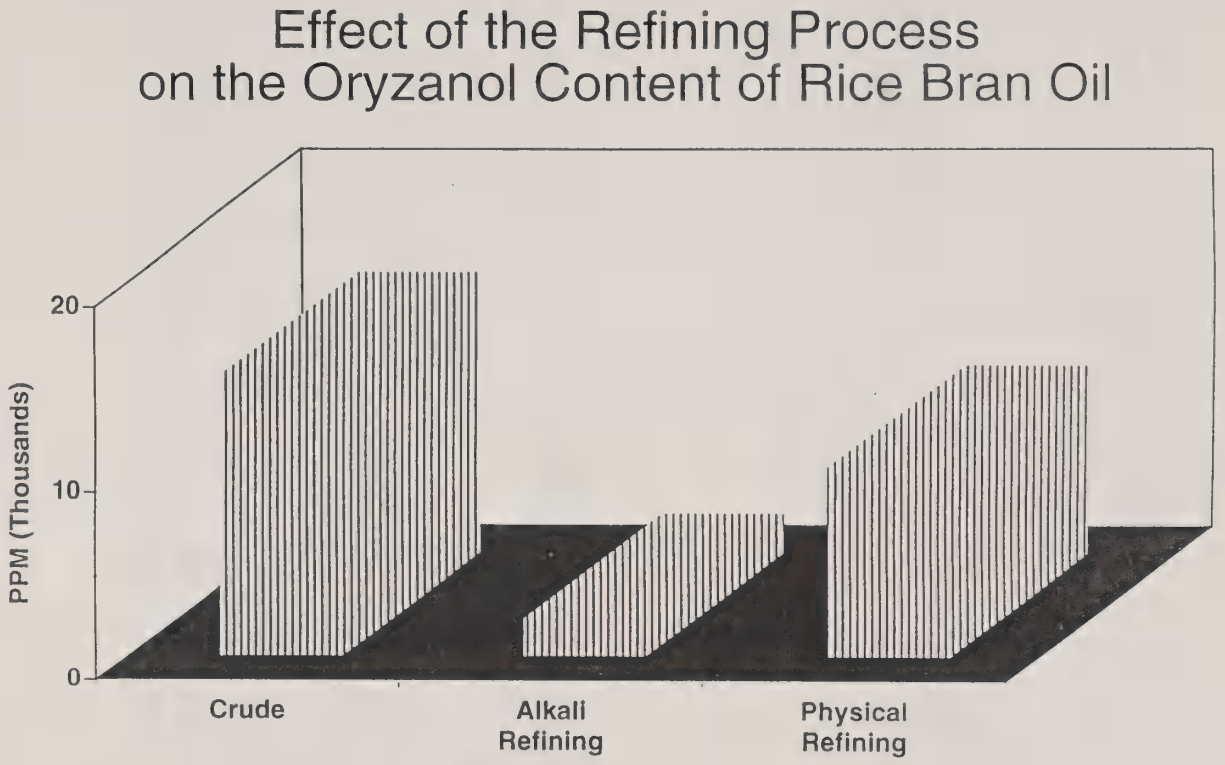
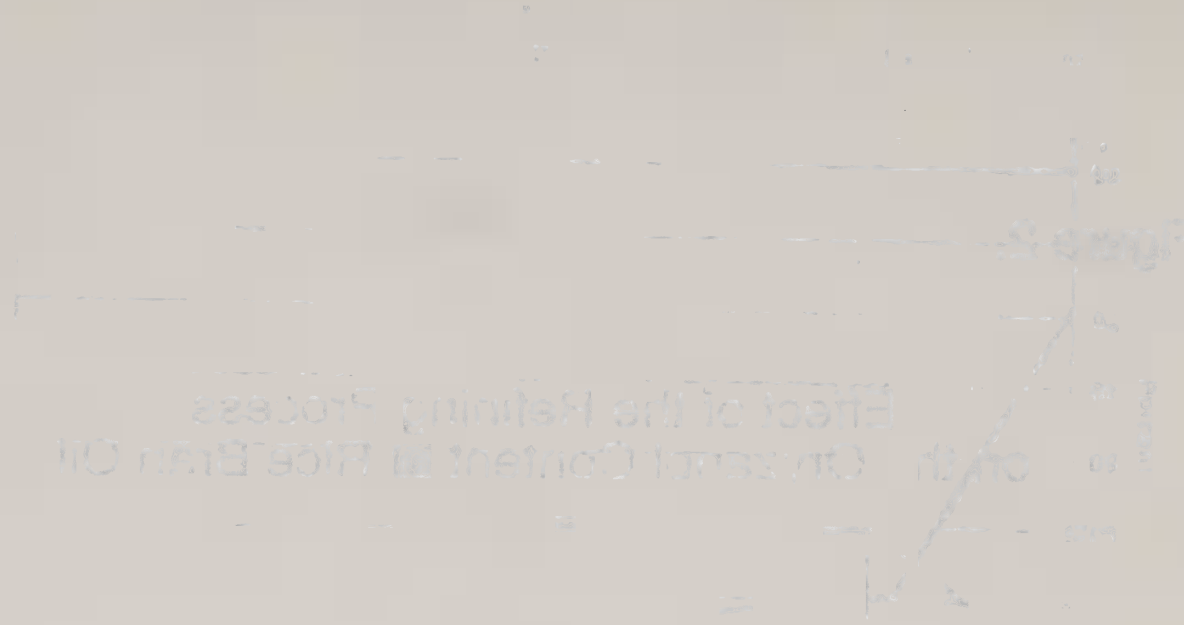

Free Fatty Acid Increase in Raw Bran
During a 135–Day Storage Period
Percent
90
80
70
60
50
40
30
20
10
0
20
40
60
80
100
120
140
Days

Figure 2.


Effect of the Refining Process
on the Oryzanol Content of Rice Bran Oil
PPM (Thousands)
20
10
0
Crude
Alkali
Refining
Physical
Refining



PROGRESS IN THE DEVELOPMENT OF A PRODUCT DIRECTED AT PREVENTING AFLATOXIN CONTAMINATION OF COTTONSEED

by

Peter J. Cotty
Research Plant Pathologist
Southern Regional Research Center
Agricultural Research Service
United States Department of Agriculture
New Orleans, Louisiana

Abstract

A strain of *Aspergillus flavus* that does not produce aflatoxins was applied to soils planted with cotton in the Yuma Valley of Arizona in order to assess strain ability to competitively exclude aflatoxin producing strains during cotton boll infection and thereby prevent aflatoxin contamination of cottonseed. In both 1989 and 1990, the atoxigenic strain displaced other infecting strains during cotton boll development. Displacement was associated with significant reductions (75% to 82% in 1989, and 99% in 1990) in the quantity of aflatoxins contaminating the crop at maturity. Although frequency of infected locules differed between years, in both years displacement occurred without increases in the amount of developing boll infection. The data suggest products to prevent contamination may be developed from atoxigenic strains. However, the economics of aflatoxin contamination is complex and these economics will dictate the course of commercial development. Currently, an Experimental Use Permit is being sought from the EPA for tests on commercial acreage

Introduction

Aflatoxins are toxic chemicals produced by certain fungi. Concern for human and animal health has led to regulatory limitations on the quantity of aflatoxins permitted in foods and feeds throughout most of the world. Aflatoxin contamination has long been a concern for several U.S. crops and for animal industries that depend on susceptible crops for feed. Whole cottonseed and/or cottonseed products are commonly fed to various livestock, including dairy cows. Aflatoxins in contaminated seed can be readily transferred to milk in slightly modified form. U.S. regulations prohibit aflatoxin concentrations over 0.5 μg/kg in milk (0.5 μg/kg = 0.5 parts per billion). Dairies producing milk tainted with unacceptable aflatoxin levels can have milk destroyed and entire operations temporarily shutdown and quarantined. To prevent unacceptable aflatoxin levels in milk, the regulatory threshold for aflatoxin B_1 in cottonseed fed to dairy cows has been set at 20 μg/kg.

Aspergillus flavus causes aflatoxin contamination of cottonseed. Populations of this fungus are highly complex and composed of many different strains (the term strain is the fungal equivalent to

an animal breed or a crop cultivar). Strains of *Aspergillus flavus* differ in ability to produce aflatoxins. In greenhouse and laboratory tests, *Aspergillus flavus* strains which do not produce aflatoxins have been shown to compete with (i.e. competitively exclude) aflatoxin-producing strains and in so doing prevent aflatoxin contamination.

Aflatoxin contamination of cottonseed can be minimized by early harvest, prevention of insect damage, and proper storage. However, even under careful management, unacceptable aflatoxin levels may occur via either unpreventable insect damage to the developing crop, or exposure of the mature crop to moisture either prior to harvest, during storage in modules, handling, transportation or even use. Competitive exclusion of aflatoxin-producing strains of *A. flavus* with atoxigenic strains of the same fungal species may provide a single method for preventing aflatoxin accumulation throughout crop production and utilization.

Two years of field studies to determine efficacy of an atoxigenic strain in preventing aflatoxin contamination of cottonseed in western Arizona indicate the potential usefulness of such strains in preventing aflatoxin contamination. The results of these studies and other aspects of commercialization of aflatoxin control products are discussed.

Methods

Inoculum preparation. *Aspergillus flavus* strain AF36, previously shown in greenhouse tests to exclude aflatoxin-producing strains competitively during infection of developing cotton bolls was used in all field tests. Inoculum was autoclaved wheat seed that had been colonized by AF36. Whole red winter wheat was autoclaved, seeded with AF36 (approximately 200,000 spores per ml) in sufficient water to bring the moisture level of the wheat to between 20 and 25% (w/w). During incubation the fungus grew in the folds of the seed and under the seed coat but, very few or no spores were produced and the appearance of the wheat remained unchanged.

Field plots. In both 1989 and 1990, at the Yuma Valley Agricultural Center near Yuma, AZ, cotton (cv. Deltapine 90) was planted in mid-March (March 9, 1989, and March 14, 1990) on a silty clay loam soil in rows on 1-m centers. In both years, fields were furrow irrigated eight times including a preplant irrigation. The experimental design in 1989 was a randomized complete block design augmented with an additional untreated control and replicated eight times. Each block contained eleven, 76-m rows of cotton and only the center row was treated. Treatments were applied to 5 m of row and were separated within the row by 15 m of untreated cotton. A second untreated control, designated control 2, was positioned in the first row of each block. In 1990 the blocks were reduced to three rows. The treated areas were 5 meters long and three rows wide and only the center row of each treatment was sampled. The blocks were separated by two untreated rows. Treatments in blocks 1, 3, 5, and 7 started 5 m into the field and were separated by 55 m of untreated cotton; treatments in replicate blocks 2, 4, 6, and 8 started 25 m into the field and were separated by 15 m of untreated cotton.

Fields used in the two years were 1.2 km apart. The field used for the 1989 test had been planted with cotton for two years immediately prior to the test and a winter fallow was maintained. In both prior years greater than 15% of the bolls were infested with pink bollworms and harvest was

delayed, permitting pink bollworm diapause. The average aflatoxin B_1 content of the cottonseed crop produced in this field exceeded 1,000 µg/kg in both prior years. Practices typical of commercial operations in the Yuma area were followed, except in order to increase both the incidence and homogeneity of aflatoxin contamination, insecticidal sprays to control the pink bollworm were not applied. Inoculum was applied prior to first bloom (May 24, 1989, and June 13, 1990) when the plants were 30 to 60 cm in height. Colonized wheat seed was spread on the soil beneath the canopy at rates of 110 g and 8.4 g per meter of row length in 1989 and 1990, respectively. On September 14, 1989 and October 25, 1990, crop was harvested by hand from a continuous segment of each replicate. All bolls on each plant were harvested, dried in a forced-air oven at 60 C for 3 days, and stored in sealed plastic bags at room temperature until analyzed.

Sorting and quantification of locules infected prior to maturation. The percent of the crop infected prior to maturation was based on the percent (by weight) of locules with bright-green-yellow-fluorescence (BGYF) (Cotty, 1991b). BGYF forms on lint and linters when Aspergillus flavus infects bolls prior to boll opening. When BGYF seed is present, it usually contains most the aflatoxin in the crop. To reduce variability among determinations of aflatoxin content, the aflatoxin contents of locules with BGYF and locules without BGYF were determined separately. In 1989, seed from the BGYF locules were delinted with a small laboratory gin and sound seeds exhibiting BGYF on the linters (small hairs not removed by ginning) were removed and divided into two portions, one for aflatoxin analyses and one for determination of the incidence of AF36. In 1990 there was a very low incidence of BGYF locules due to low pink bollworm damage. Therefore, BGYF locules were not processed with a gin. Instead, a single sound seed was removed from each BGYF locule for fungal isolations and the remainder of each locule was analyzed individually for aflatoxin content.

Aflatoxin content of the crop. In 1989, 25-g portions of whole, ginned, BGYF cottonseed were pulverized and extracted. For the 1990 test, the same technique was used as for the 1989 test except, infected whole locules (minus the single seed used to isolate the infecting strain) were extracted individually

Monitoring strain distribution. The incidence of the applied strain was determined with genetic tests as previously described (Bayman & Cotty, 1991 & 1993).

Quantification of fungal populations. Populations of *A. flavus* in the soil both one day prior to application of treatments and one day after harvest were enumerated in 1989 and 1990. In 1990, the quantity of *A. flavus* superficially associated with the mature crop at harvest was also determined.

Results

Incidence of BGYF. In 1989 there was a great deal of pink bollworm damage (over 30% of the bolls were infested) and subsequent infection of developing bolls by *A. flavus* resulted in a high percent of locules (22 $\pm$ 2 % by weight) that were positive for BGYF. In 1990, there was little pink bollworm damage (less than 5% of bolls were infested) and there were relatively few locules

with BGYF (0.9 ± 0.1 %). In both the 1989 and 1990 tests, the percent of locules infected prior to boll maturity (BGYF locules) did not differ significantly ($P = 0.05$) among treatments.

Aflatoxin content of the crop. In both years, BGYF seed from wheat-treated plots contained significantly less aflatoxin B_1 than BGYF seed from untreated control plots. The aflatoxin B_1 content of the BGYF seed was 75 to 82% lower than the controls in 1989 and 99.6% lower in 1990. In 1989, the quantity of toxin in the seed not exhibiting BGYF was also determined. Only 2.6% of the detected aflatoxin occurred in seed not exhibiting BGYF.

The quantity of aflatoxin B_1 in the BGYF seed from the 1989 crop was inversely correlated with the percent of isolates from that seed belonging to the applied atoxigenic strain (Figure1). Replicate blocks containing high incidences of the applied strain had low aflatoxin content and vice versa. Complete analyses were successfully performed on a total of 34 locules exhibiting BGYF on the lint in 1990. Only one of 18 locules from which the applied strain was isolated contained detectable quantities of aflatoxins. However, aflatoxin was detected in 13 of 16 locules (81%) from which an isolate not belonging to the applied strain was isolated. Locules from which the applied strain was isolated contained significantly ($P = 0.05$ by Student's *t*-test) less aflatoxin than locules from which other strains were isolated (200 parts per billion versus 65,900 parts per billion). Most locules (63%) from which other strains were isolated contained over 10,000 PPB.

Strain distribution. Prior to the test, the applied strain was 1 of 48 individuals in 1989 and 1 of 36 individuals in 1990. By contrast, the overall frequency of the strain within *A. flavus* soil populations increased by harvest ($P = 0.05$ by the paired t-test) to 42% and 63% in 1989 and 1990, respectively.

The applied strain was a major component of the *A. flavus* population infecting the crop during boll maturation (identified via bright-green-yellow-fluorescence, BGYF). Although the applied strain was isolated from a greater percent of the infected bolls from treated plots than from infected bolls from untreated controls, the applied strain was isolated from portions (25% and 7% in 1989 and 1990, respectively) of infected bolls from untreated plots in both years. In 1990, the applied strain was isolated from all bolls exhibiting BGYF and harvested from the wheat treated plots. The incidence of the applied strain within populations of *A. flavus* resident on the surfaces of seed-cotton at harvest was determined in 1990. Seventy-five percent of isolates from seed-cotton surfaces from plots treated with colonized wheat seed in 1990 belonged to the applied atoxigenic strain.

Magnitude of fungal populations. The quantity of *A. flavus* on the surface of the seed cotton at harvest was quantified in 1990. Counts of propagules of *A. flavus* from seed harvested from treated and control plots 1990 did not differ significantly. In 1989 and 1990, soil populations exceeded 1,000 propagules per gram prior to application of treatments and increased ($P = 0.05$ by paired t-test) in all treatments between application and harvest.

Discussion

In two years of field tests in the Yuma Valley of Arizona, soil application of an atoxigenic strain of *Aspergillus flavus* on colonized dead wheat seed resulted in a reduced quantity of aflatoxins in the cottonseed crop at maturity without an increase in the incidence of infection, as measured by BGYF. Analysis of fungal populations infecting the crops in both years provided evidence that these reductions were associated with displacement of the resident aflatoxin producing *Aspergillus flavus* population by the applied atoxigenic strain.

The quantity of aflatoxin in wheat treated plots was 75% to 82% less than in untreated controls in 1989 and 99.6 % less in 1990. However, the applied strain was isolated from 25% and 7% of infected seed in the untreated control plots in 1989 and 1990, respectively. Therefore, aflatoxin levels in control plots were probably lowered by atoxigenic strain applications and the control of aflatoxin B_1 contamination associated with the application of colonized wheat seed is probably underrepresented, especially for 1989. The correlation between incidence of the applied VCG and aflatoxin content of infected seed (Figure 1) may better describe the impact of the atoxigenic strain on contamination. As displacement of aflatoxin-producing strains increased (and the percent of the applied strain increased), the quantity of aflatoxin in the crop decreased.

Although the rate of application of wheat infested with the biocontrol agent in 1989 was greater than in 1990 (110 g/m row length versus 8.4 g/m row length), the percent of the applied strain in infected locules from treated plots was only 67% in 1989 versus 100% in 1990. Lower displacement in treated plots in 1989 may have resulted from failure to treat rows adjacent to rows sampled at harvest; in 1990 rows on each side of the sampled rows were treated. Higher rates of displacement in 1990 with lower application rates more broadly dispersed may indicate that useful displacement and associated aflatoxin reductions can be achieved with much lower rates uniformly applied over larger contiguous areas. Data from subsequent field tests in 1991, 1992, and 1993 (data not reported) suggest application of 5 pounds of colonized wheat seed per acre will provide significant reductions in aflatoxin contamination.

The incidence of the applied VCG in infected seed from untreated control plots was much greater in 1989 than in 1990 (25% versus 7%). The crop was treated later with less material in 1990 than in 1989 and reduced spread may have resulted from a combination of lower inoculum, a larger canopy at application and environmental differences. It is surprising that in 1989, even though only 1.2% of the experimental field was treated (if the amount of wheat applied had been dispersed over the entire plot, the application rate would have been 5.9 pounds per acre), the average incidence of the applied strain was over 25% at the points most distant from applications.

The rate at which the applied strain displaced aflatoxin producing strains, in both years, suggests initial colonization of developing crops may greatly influence which fungal strains predominate during crop development. Introduction of new, uncolonized resources in the form of a crop uniformly developing may provide the opportunity for rapid swings in the composition of certain fungal populations associated with crops through colonization and establishment by relatively few initial strains. This phenomenon of epidemic increases in a few fungal types may occur frequently

in agricultural fields. Such increases have been observed in unmodified *A. flavus* populations (Bayman & Cotty, 1991).

The amount of infected developing cotton bolls did not differ between treated plots and untreated controls in either year. Predisposition of developing bolls (i.e. through insect activity) may be a greater determinant of infection rate than the quantity of inoculum to which the crop is exposed. This may be particularly true in the desert valleys of Arizona where crops frequently are dusted by soil dispersed by agricultural activities and wind. This dust contains large quantities (at times exceeding 5,000 propagules/m^3 of air) of *A. flavus* inocula. Furthermore, during the cotton season, very large proportions of dead and necrotic plant and animal tissue become colonized by *A. flavus* and these contribute to inoculum levels. Thus, cottonbolls produced in these areas become exposed to large concentrations of *A. flavus* inocula.

The population of *A. flavus* on seed cotton surfaces at harvest in 1990 did not differ among treated and control plots and the applied strain contributed only a minor portion (4%) of the propagules in the control plots and most (75%) of the propagules in the treated plots. It is therefore apparently possible to exclude resident aflatoxin producing strains without causing overall population increases. Exclusion apparently occurred during the *A. flavus* population increase which resulted in high propagule counts (over 20,000 propagules per gram) on the crop at harvest. The quantity of the fungus associated with the crop appeared to be dependent on a factor other than the quantity of fungus present early in the season when the colonized wheat was applied.

Complete details of the 1989 and 1990 field plot studies were recently published in a journal article (Cotty, 1994b).

Economics limiting development of aflatoxin control products dictate certain constraints on the process of bringing products based on atoxigenic strains to commercial use. From the grower's economic perspective, aflatoxin contamination is not a quantitative variable like yield. For example: fifty percent reductions in certain pests (that act as quantitative variables) will result in 20% to 30% increases in yield with corresponding increases in the value of the crop produced. However, 50% reductions in aflatoxin contamination may have no value if the resulting seed contains over 20 parts per billion. Seed above 20 PPB is discounted because it can not be sold to dairies. Thus, treatments that reduce contamination but, still result in seed above 20 PPB, have no value.

Loss resulting from unacceptable aflatoxin levels differs over the cotton belt. In our target area, western Arizona, the cost varies roughly from $20 to $35 a ton or about $20 to $35 an acre. We hope to produce materials for atoxigenic strain applications for $5.00 per acre or less. If treatments are 70% effective and an average of 40% to 70% of seed is above 20 PPB and the benefit of having aflatoxin free seed is $20 to $40 a ton then growers will gain an average return above an initial $5/acre investment of $0.60/acre to $14.60/acre (Table 1).

There may be long term benefits from atoxigenic strain applications resulting from strain ability to remain in fields until the next crops are planted. Thus, the average efficacy of treatments over

multiple years would be greater than when applied in a single season. Furthermore, benefits are gained by portions of the community other than the cotton producer. The fungi which produce aflatoxins remain with the crop until use and a risk of increased contamination occurs during transit and storage. The risk of contamination remains even when the crop is in the hands of the end user. The cost of contamination is greatest when aflatoxin is not detected until it is in the milk. Like the aflatoxin producing strains, the applied atoxigenic strains will stay associated with the crop until use. This means crops have protection until use. As the stigma of aflatoxin contamination is removed, the ability to market seed and meal from affected areas may increase. In areas where multiple crops are affected by contamination (i.e. corn, cotton, and peanuts), treatments to one crop may benefit all crops. Thus, economics of applications in such areas is more complicated. Community-wide benefits may permit application of atoxigenic strains outside of our target area, once economic and logistic feasibility has been established.

Just as the dust does not stay in the field in which it is raised, fungi do not stay in the field to which they are applied. Thus, applications may be expected to reduce contamination risk in nearby fields over time. Similarly, aflatoxin producing strains will blow in and continuously inoculate treated fields. Therefore, although atoxigenic strain applications have been very effective in small plots, the best results will be obtained with the largest treated area..

Development of a product based on atoxigenic strains and sold as an agrochemical would probably be the simplest course to producing a commercially useful aflatoxin control product. However, the initial acreage on which atoxigenic strains could be applied may be too small to warrant significant investment by an agrochemical company. Alternatives to development by an agrochemical company may include development of either a Pest Control District or a Regional Aflatoxin Elimination Program. Such programs may have the advantage of being tailored to the specific region, being more cost effective, and providing an avenue through which fungal populations may be monitored independently of aflatoxin levels

Regardless of the means of intervention employed, there will be fungi associated with crops. Dead, weakened, and partially decayed plant tissues are readily available in agricultural environments, and it is not feasible to prevent utilization of these resources by fungi. A level of control over which fungi become associated with crops may be permitted by the seeding of select fungal strains into agricultural fields in a manner similar to the seeding of plants. Such strains may be selected for adaptation to the crop ecosystem, reduced quantities of traits detrimental to human activity, and increased traits considered beneficial. This process of fungal domestication may permit minimization of certain problems caused by fungi (*i.e.* mycotoxin contamination) and optimization of beneficial fungal traits (*i.e.* degradation of crop debris). Currently an Experimental Use Permit (EUP) from the U. S. Environmental Protection Agency is being sought. An EUP is required in order to perform tests on commercial acreage. We are asking to treat commercial acreage during the 1996 cotton season.

Acknowledgments

This work was made possible by the cooperation and assistance of the Yuma Valley Agricultural Center, University of Arizona. The author thanks Mrs. Darlene Downey for technical assistance and the National Cottonseed Products Association for funding the required travel.

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Table 1. Influence of the percent of fields with unacceptable aflatoxin contamination, the cost of contamination, and product efficacy on the return of a $5.00/acre investment in an aflatoxin control measure

Contaminated (%)	Differential value ($/acre)	Average cost ($/acre)	Efficacy (%)	Treatment value ($/acre)	Average return ($/acre)
70	15	10.5	90	9.45	4.45
70	20	14	90	12.6	7.6
70	25	17.5	90	15.75	10.75
70	15	10.5	70	7.35	2.35
70	20	14	70	9.8	4.8
70	25	17.5	70	12.25	7.25
70	15	10.5	50	5.25	0.25
70	20	14	50	7	2
70	25	17.5	50	8.75	3.75
50	15	7.5	90	6.75	1.75
50	20	10	90	9	4
50	25	12.5	90	11.25	6.25
50	15	7.5	70	5.25	0.25
50	20	10	70	7	2
50	25	12.5	70	8.75	3.75
50	15	7.5	50	3.75	-1.25
50	20	10	50	5	0
50	25	12.5	50	6.25	1.25
30	15	4.5	90	4.05	-0.95
30	20	6	90	5.4	0.4
30	25	7.5	90	6.75	1.75
30	15	4.5	70	3.15	-1.85
30	20	6	70	4.2	-0.8
30	25	7.5	70	5.25	0.25
30	15	4.5	50	2.25	-2.75
30	20	6	50	3	-2
30	25	7.5	50	3.75	-1.25

Contaminated = Average percent of the crop contaminated with ≥20 ppb aflatoxins in a given year (on a gin wide basis).
Differential Value = difference between value of seed below 20 ppb aflatoxins and value of seed ≥20 ppb.
Average Cost = average revenue loss per acre (on a gin-wide basis) if crop has over 20 ppb aflatoxin.
Efficacy = percent treated acres with less than 20 ppb where aflatoxin would otherwise exceed 20 ppb.
Treatment Value = average amount of value added to the crop by treating.
Average Return = per acre; assumes cost of application of $5.00 per acre.

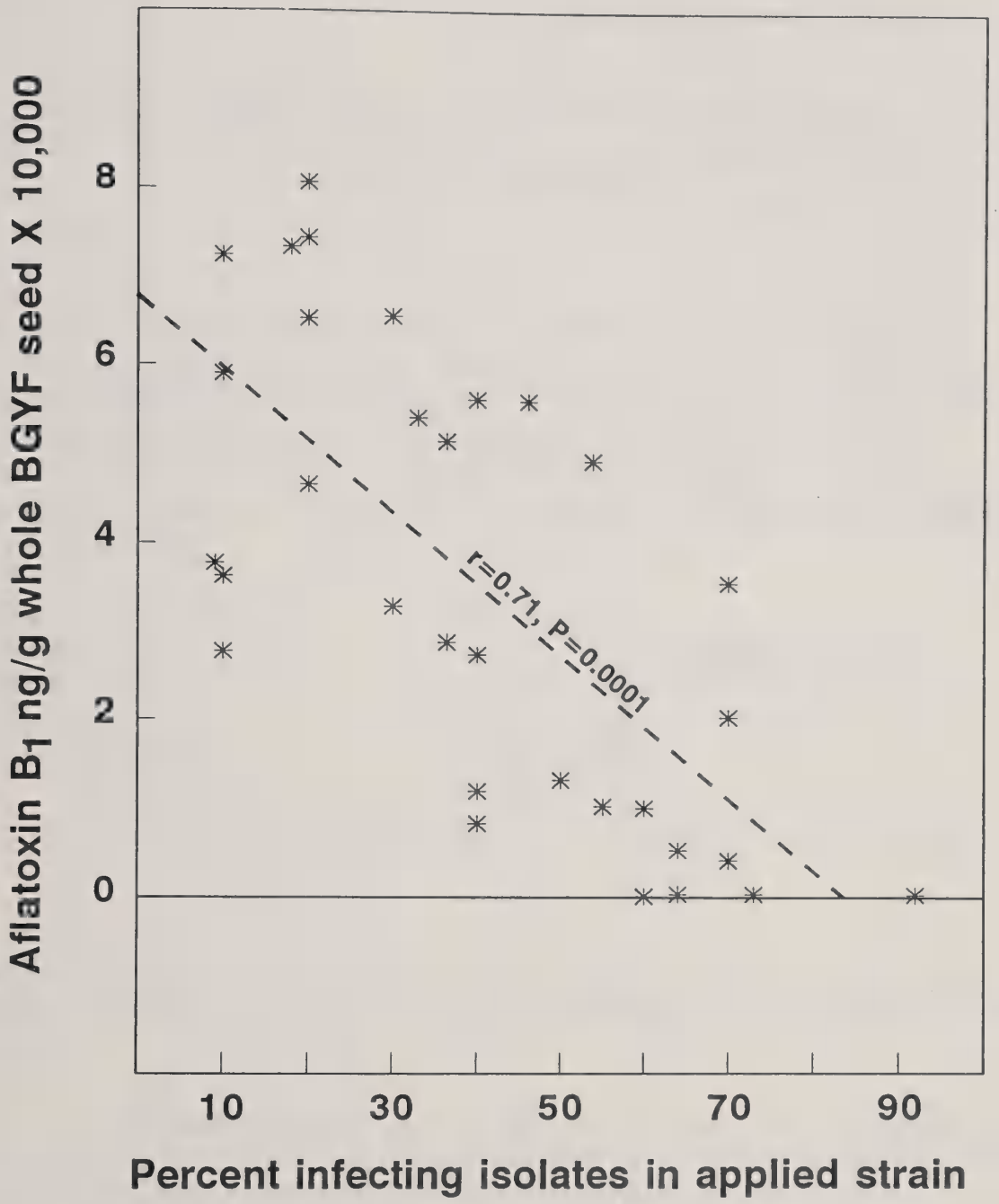

Figure 1. Correlation of the incidence of the applied strain among isolates internally infecting BGYF seed in 1989 and the quantity of aflatoxin B_1 detected within that seed. Each point represents the average for a replicate plot.

COMPARATIVE RISK ASSESSMENT OF n-HEXANE, COMMERCIAL HEXANE AND OTHER HYDROCARBON SOLVENTS.

by

Jennifer B. Galvin,[1] Carroll J. Kirwin,[1] and Daniel W. Kelly.[2]
[1]Phillips Petroleum Co., 4th and Johnstone, Bartlesville, OK 74004;
[2] Dow Corning Co., Midland, MI

Chronic inhalation exposure to n-hexane at greater than 100 ppm can cause progressive nervous system dysfunction. Due to the nerve toxicity exhibited by n-hexane, its permissible exposure limit (PEL) for a worker was set at 50 ppm. Other similar chemicals have been tested for their potential to cause nerve damage; however, none have been found as potent as n-hexane. Hence their PELs reflect they are less toxic and allow the worker to be exposed to more (higher PEL) of the chemical. For example:

Chemical	PEL (ppm)
Isohexane	500
Heptane	400
Cyclohexane	300
Commercial Hexane	To be established

In summary, other solvents are available that are not the worker health concern that n-hexane is.

Commercial hexane has a toxic aspersion cast on it because it contains 52-67% n-hexane. However, commercial hexane does NOT cause neurotoxicity as does pure n-hexane.

The oilseed extraction industry uses commercial hexane to extract valuable oils from various seeds. This commercial hexane is made up of various C-6 isomers. The product that the EPA mandated testing on was 52% n-hexane, 16% methylcyclopentane, 16% 3-methylpentane, 13% 2-methypentane and 3% cyclohexane. The major concern with this mixture was that it might be neurotoxic like its major component n-hexane. However, male and female rats inhaling 900, 3000 or 9000 ppm commercial hexane for 13 weeks showed no neurotoxic effects at any of the dose levels. Treated animals demonstrated similar behavior to controls in the motor activity test and neuropathological studies at all levels of the neuroaxis proved negative. In conclusion, the no observed adverse effect level (NOAEL) for the nervous system is at least 9000 ppm.

Another short term inhalation study was performed at the same test levels to evaluate an animal's ability to respond to a learned behavior. The data revealed no significant differences in the rate of response between control and commercial hexane treated groups. In conclusion, commercial hexane does not cause toxic effects to the nervous system of rats as evaluated by these tests.

How does this compare to the neurotoxicity of n-hexane? Rats inhaling 500 ppm n-hexane (22 hrs./day, 7 days/wk.) showed giant axonal nerve degeneration after only 8 weeks of exposure.[1] At lower doses, a 34-week inhalation study showed a no adverse effect level for n-hexane to be 125 ppm. However, neurologic effects were seen at 200 ppm. Humans, are the more sensitive species, specifically in the case of n-hexane, since they metabolize n-hexane to the neurotoxin, 2,5 hexanedione. The sensitivity of humans is proposed because of the high content of 2,5-hexanedione found in human urine. The neurotoxicity of this metabolite was shown by Spencer and Schaumberg.[2] The primary metabolites of n-hexane in the rat is 2-hexanol with lesser amounts of 2,5-hexanedione. (A comprehensive review of the toxicity of n-hexane can be found in reference 3).

Isohexane is a blend of six carbon isomers which include:

2-methylpentane (isohexane)
3-methylpentane
neohexane (2,2-dimethylbutane)
2,3-dimethylbutane

This mixture has not been tested extensively, but Sandmeyer[4] stated after exposure to high concentrations of hexane isomers, mucous membrane irritation would be expected. Isohexane is predicted to cause narcosis and is a documented cardiac sensitizer. However, based on structure metabolism relationships, it is not expected to produce neurotoxicity since 2,5 hexanedione is not a product of its metabolism. Acute toxicity tests show the isohexane mixture to have an LC_{50} >3125 ppm. Respiratory tract irritancy was not found when animals were exposed to 3250 ppm.[5]

Individual Components of isohexane have been tested for their ability to cause neurotoxicity.[6] This report stated, "The methylcyclopentane, 2- and 3-methylpentane groups had some signigicant differences in comparisons with the controls, although these differences were not so distinct as those in the n-hexane group." This study involved giving the chemicals orally to the animals which is not a relevant route of exposure for the workplace. Also, it is important to remember isohexane is a blend of chemicals and much like commercial hexane is probably not metabolized to the neurotoxicant, 2,5 hexanedione.

Cyclohexane is the subject of an EPA TSCA Section 4 test rule which will result in a considerable toxicology data base being generated. Until this testing is done, there is a limited amount of neurotoxicity data on this chemical. In a detailed investigation, Frontali and co-workers failed to find morphological evidence of neuropathy in rats subchronically exposed to cyclohexane. Therefore, cyclohexane is not judged a neurotoxicant.[8]

Heptane produces narcosis at concentrations of 10,000 to 15,000 ppm. These signs of central nervous system involvement occurred in the absence of noticeable mucous membrane irritation. There are spurrious older accounts [9,10] indicating heptane was part of a mixture that caused neurotoxic effects in workers. However, these reports have been questioned because heptane is not metabolized to the neurotoxic 2,5 hexanedione. Heptane is not judged to be a neurotoxicant at this time.

In conclusion, the only hydrocarbon mentioned in this report that has been convincingly demonstrated neurotoxic in both animals and humans is n-hexane. Surprisingly, commercial hexane (52% n-hexane) did not produce neurotoxicity in subchronic inhalation studies and hence is not a neurotoxicant based on these studies. In comparing all the toxicities of the hydrocarbons, they all produce reversible CNS effects at high concentrations, but only n-hexane is a neurotoxicant. Therefore, the use of commercial n-hexane is judged as safe for workers as isohexane, heptane or cyclohexane. No benefits from lowered worker exposures would be derived by switching to a different hydrocarbon.

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HYDROCARBON SOLVENTS FOR OILSEED EXTRACTION -- REGULATORY CONCERNS

by

Phillip J. Wakelyn
Manager, Environmental Health and Safety
National Cotton Council of America
Washington, DC

Abstract

Environmental and workplace regulations impact the users of hexane and other hydrocarbon solvents for extraction of cottonseed and other oilseeds. Some alternate hydrocarbon solvents to hexane for oilseed extraction have less regulatory requirements. Environmental Protection Agency (EPA) standards cover clean air [criteria pollutants (ozone formed by oxidation of VOC's), air toxics (hexane)]; clean water (waste water, storm water); solid and hazardous waste; Emergency Planning and Community Right-to-Know; and toxic substances control. The Occupational Safety and Health Administration (OSHA) regulates permissible exposure limits (PELs) for hexane, hexane isomers and some other hydrocarbons; process safety management; hazard communication; personal protective equipment for flammable liquids and so forth. Some of the more important regulations and government actions and their impact are discussed.

Introduction

Hexane has been the solvent used for oilseed extraction for a long time. Many workplace and environmental regulations apply to the use of hexane as well as to other potential replacement solvents for hexane in oilseed extraction. In addition to possibly having less workplace and environmental requirements, alternate solvents may improve quality, be more energy efficient and have other benefits.

This paper will review some of the regulatory requirements for hydrocarbon solvents used for oilseed processing.

OSHA -- Workplace Requirements

The Occupational Safety and Health Administration (OSHA) has been in existence since 1971 when it was formed as part of the requirements of the Occupational Health and Safety Act of 1970 (P.L. 91-596, December 29, 1970, effective April 28, 1971). The original health and safety standards were brought in by reference as national consensus standards or existing federal standards. For example, the current list of permissible exposure limits (PELs) came in from the Walsh Healey Act as national consensus standards. Since 1971, OSHA has promulgated many more health and safety standards, under Section 6(b) of the Act.

Air Contaminants (29 CFR 1910.1000): An employee's exposure to substances listed under this standard are limited to the level listed in Table 1 of the standard (see Table 1 in this paper which lists the PELs for the solvents.) The PEL listed for a substance is an 8 hour time weighted average exposure. To achieve compliance with the PEL, administrative or engineering controls must first be determined and implemented whenever feasible. When such controls are not feasible to achieve full compliance, protective equipment or any other protective measures are to be used to keep exposure of employees within the PEL.

On January 19, 1989, OSHA issued a new revised standard for air contaminants which included additional PELs for 164 new toxic substances and more protective PELs for 212 substances. Included was a standard for hexane, which was lowered to 50 parts per million (ppm) from 500 ppm and a PEL for hexane isomers of 500 ppm (1,000 ppm short-term limit). The effective date of the final rule was March 1, 1989. Employees were required to comply with all PELs by engineering control where feasible by December 31, 1992. However, in September 1992, the court overturned this rule. The PELs that officially apply are the ones that were adopted in 1971. Since most of the PELs that were changed are at the lower level in the American Conference of Governmental Industrial Hygienist (ACGIH) list of threshold limit value (TLVs) and industry is already complying with the hexane and hexane isomer standards, the new levels are the levels that it would be prudent to comply with.

Hazard Communication Standard (HCS; 29 CFR 1910.1200): The OSHA hazard communication standard covers all industries including oil mills. It requires information on hazardous chemicals to be transmitted to employees through labels, material safety data sheets (MSDS), and training programs. A written hazard communications program and recordkeeping are also required.

Chemical manufacturers and importers are required to review the available scientific evidence concerning the hazards of the chemicals they produce or import, and to report the information they find to their employees and to manufacturing employers who purchase their products. Oil mills do not have to prepare MSDSs since they are not chemical manufacturers or importers, but they should request MSDSs from suppliers for any hazardous materials they use. Downstream employers such as oil mills can rely on the evaluation performed by the chemical manufacturer or importer to establish their hazard communication programs. Hexane and all the potential replacements solvents listed in Table 1 most likely would require MSDSs.

Process Safety Management (PSM; 29 CFR 1910.119): All facilities that have one or more of 137 listed chemicals above their threshold quantities or those who have 10,000 pounds or more of a flammable liquid or gas [as defined by the Hazard Communication Standard -- "Liquid, flammable means any liquid having a flashpoint below 100°F (37.8°C), except any mixture having components with flashpoints of 100°F (37.8°C) or higher, the total of which make up 99% or more of the total volume of the mixture"-- this includes hexane,

hexane isomers and all hydrocarbon solvents in Table 1] as part of a process are covered by this standard.

The regulation went into effect on May 26, 1992. The major exceptions to the May 26, 1992 implementation date are the requirements for a five year Process Hazards Review schedule and for a formal audit every three years. For oil mills, all elements except the formal audit due in May of 1995 should be in place.

In addition to the PSM standard, OSHA has been enforcing two other regulations for operations of processes with flammable liquids. Under Personal Protective Equipment - General Requirements (29 CFR 1910.132), OSHA has cited or obtained voluntary agreement from organizations relative to flame resistent clothing. Operators and other employees working in the area of a flammable process are being required to wear flame resistant work clothing. [OSHA compliance officers have used the term "Nomex clothing" in their compliance correspondence. This is not correct as there are a number of materials which perform equally to or better than Nomex, such as Flame Resistant cotton (FR-cotton).] It appears to be prudent for oil mills who use hexane or other flammable solvent extraction processes to require FR-cotton clothing for all operations related personnel.

A second related safety regulation falls under Fire Brigades (29 CFR 1910.156). Specifically, OSHA has cited organization for failure to meet standards such as: (1) training, both initial and annual refresher training; (2) protective equipment availability and testing; and, (3) fitness for duty including periodic physicals. If an on-site fire brigade is part of the site's Emergency Response Plan, then these requirements must be also met. In addition, the requirement of the PSM standard for an Emergency Response Plan triggers the requirements of Emergency Action Plan, 29 CFR 1910.38(a).

EPA--Environmental Requirements

The role of the U.S. Environmental Protection Agency (EPA) is to protect human health and welfare and the environment. Many laws have been enacted to address releases or threats of releases of hazardous substances. EPA regulates all aspects affecting the environment--the legislation that serves as the basis for the regulations can be divided into the following categories:

- Statutes that are media-specific (Clean Air Act and Clean Water Act);
- Statutes that manage solid waste (Resources Conservation and Recovery Act [RCRA] and Comprehensive Environmental Response, Compensation and Liability Act [Superfund]); and
- Statutes that directly limit the production rather than the release of chemical substance (Toxic Substances Control Act [TSCA] and Federal Insecticide, Fungicide and Rodenticide Act [FIFRA]).

See Table 2 for an overview of requirements that apply to each solvent.

Clean Air Act (CAA; 40 CFR 51-99): The CAA was amended in 1990 (PL 101-549, Nov. 15, 1990) and these amendments greatly expanded the Act. To satisfy the CAA requirements states are required to implement regulations and develop state implementation plans (SIPs). Federal and state clean air regulations are administered by the EPA and enforced by state air control boards. The CAA regulates through establishment of emission standards. Criteria pollutants are regulated as National Ambient Air Quality Standards (NAAQS) and hazardous air pollutants (HAP) as National Emission Standards for Hazardous Air Pollutants (NESHAP).

EPA has set NAAQS for six criteria pollutants, ozone, sulfur dioxide, carbon monoxide, particulate matter (now PM-10), nitrogen oxides, and lead, under sections 108 and 109 of the Clean Air Act. (PM-10 particles are particulates 10 microns in size and smaller.) The NAAQS are set at levels sufficient to protect public health with an adequate margin of safety. EPA set emission standards for seven toxic air pollutants under Section 112 of the CAA from 1978 to 1990. The 1990 amended act expanded the list of HAPs (air toxics) to 189 substances including hexane and more strictly regulates nonattainment areas for criteria pollutants.

- Nonattainment, Title I: Hexane and all of the alternate solvents would be considered volatile organic compounds (VOCs), which can undergo photochemical oxidation in the atmosphere to form ozone (40 CFR 51.100). Oil mills, most likely would be major sources of VOCs (over 100 tons release in attainment areas) and would be covered by the requirements for ozone emissions and attainment. If facilities are in ozone non-attainment areas, facilities could be required to reduce emissions (Reasonable Achievable Control Technology; RACT).

- Hazardous Air Pollutants (HAP) or Air Toxics, Title III: HAP relates to whether an operation in an emitter of any of the 189 chemicals on the list. Hexane is on this list, but none of the potential alternate solvents is. Oil mills would be a major source of hexane -- 10 tons per year or 25 tons per year of total HAPs. EPA established a list of source categories and subcategories for the 189 HAPs for the purposes of promulgating technology-base standards (57 FR 31576; July 16, 1992) and the Administrator proposed the schedule of dates for promulgating standards for each category or subcategory of sources (58 FR 42760; Aug. 11, 1993). The air toxic requirements of the CAA 1990 for establishing control measures for source categories are: technology-based emission standards established for major sources will require the maximum degree of reduction in emissions, taking costs and other health and environmental impacts into account. Standards are to be set based on known or anticipated effects of pollutants on the public health or the environment, the quantity emitted, the location of emissions and the efficiency of growing categories and subcategories. Compliance will involve the installation of what will be determined as the Maximum Achievable Control Technology (MACT). MACT will be at least as stringent as the average emissions limitation achieved by the best controlled 12 percent of similar sources. MACT standards for vegetable oil processing using hexane are due November 15, 2000.

Once a standard has been promulgated for a source category, then a source will have three years in which to comply. For new sources, MACT will be at least as stringent as the most stringent emissions level achieved in practice by a similar source. MACT standards will be reviewed and revised if necessary at least every eight years. If EPA determines that a significant risk remains after the MACT controls are applied, then EPA must issue "residual risk standard" (health-based standards) within eight years after MACT is promulgated.

• Title III, Section 112 (r): Sec. 112(r) is for the prevention of chemical accidents and addresses the same concerns as the OSHA PSM standard but different chemicals are covered. The goals are to focus on chemicals that pose a significant hazard to the community should an accident occur, to prevent their accidental release to minimize the consequences of such releases. The list of chemicals covered is composed of three categories: a list of 77 toxic substances, a list of 63 flammable substances, and explosive substances with a mass explosion hazard as listed by the U.S. Department of Transportation. Isopentane and pentane are on the list of flammable substances but not hexane and hexane isomers or the other hydrocarbon solvents. So this dos not appear to affect hexane or any of the potential alternative solvents.

• Title V, Permits: All major sources of regulated pollutants are required to have federal operating permits (FOP). FOP require a lot of paper work and fees are about $25 per tons of all regulated pollutants emitted by a facility.

Resource Conservation and Recovery Act (RCRA; 40 CFR 260-280): RCRA is a "cradle-to-grave" regulatory system for hazardous waste. The act requires generators, transporters, and disposers to maintain written records of waste transfers, and requires EPA to establish standards, procedures and permit requirements for disposal. The act also requires states to have solid waste management plans, prohibits open dumping, and required EPA to establish criteria for sanitary landfills.

• Toxic Characteristics Leaching Potential (TCLP): This is a list of about 30 substances that has to be tested to determine that they are not leachable from a waste. None of the solvents are on this list.

• Hazardous waste: Waste with characteristics of ignitability, corrosivity, reactivity and toxicity. Only cyclohexane is on this list.

Toxic Substances Control Act (TSCA; 40 CFR 702): Requires EPA to review the health and environmental effects of new chemicals (referred to as "Premanufacturing Notice" or "PMN") and chemicals already in commerce. If a chemical's manufacturer, processing, distribution, use or disposal would create unreasonable risks, EPA can regulate or ban it. All new toxicological data of effects of chemical not previously mentioned must be reported. It is not anticipated that any of the solvents would have requirements under TSCA unless

new data become available. New toxicological information on hexane has been reported to EPA in the last 2 years.

Emergency Planning and Community Right-to-Know Act (EPCRA/SARA Title III; 40 CFR 355-370): Enacted as Title III of the 1986 Superfund Amendments and Reauthorization Act ("SARA"), the act requires states to establish emergency planning districts with local committees to devise plans for preventing and responding to chemical spills and releases. [Superfund is the Comprehensive Environmental Response, Compensation and Liability Act of 1980, which gives EPA authority to force those responsible for hazardous waste sites or other hazardous substance releases to conduct cleanup or other response actions.] The law also requires facilities to file reports on certain dangerous chemicals they handle or release to the environment. The reports are to aid emergency planning and let communities and regulators know about potential hazards.

- Sec. 302 -- for chemicals designated as extremely hazardous substances (EHS), facility must cooperate with state and local planning officials in preparing comprehensive emergency plans; none of the chemicals are on this list.

- Sec. 304 -- facilities must report accidental release of EHSs; hexane and cyclohexane have reportable quantities for spills.

- Sec. 311, 312 -- businesses must make MSDSs, for chemicals which are required to have MSDSs, available to state and local officials; this would cover all of the chemicals since all would have MSDSs.

- Sec. 313 -- (Toxic Reporting Inventory - TRI) businesses are required to report releases to air, water and land of the chemical on the Sec. 313 list. Hexane has recently been added to the TRI list with reporting due July 1, 1996 (59 FR 61488; November 30, 1994). Cyclohexane and isopropyl alcohol are also on the list. TRI reporting requirements are triggered if a facility manufacturers, processes or uses a listed substance in a quantity above the statutory threshold of 10,000 or 25,000 lbs./year.

Summary

In summary, some of the potential alternate solvents to hexane would have less environmental and workspace requirements than hexane.

Table 1. OSHA (Workplace) Regulations*

Chemical Name (CAS No.)	PEL [Health Risk]
n-hexane (110-54-3)	500 ppm/1800 mg/m^3 (new PEL was 50 ppm); [neuropathy]; ACGIH (TLV) 50 ppm/180 mg/m^3 (same as new PEL)
n-heptane (142-82-5)	500 ppm/200 mg/m^3; [narcosis]; new PEL was 400 ppm, 500 ppm STEL same as ACGIH (TLV)
cyclohexane (110-82-7)	300 ppm/1050 mg/m^3; [sensory irritation]; ACGIH (TLV) same
cyclopentane (287-92-3)	None (new OSHA PEL was 600 ppm); [narcosis]; ACGIH (TLV) 600 ppm
hexane isomers (none)	None (new OSHA PEL was 500 ppm TWA; 1000 ppm STEL); [narcosis]; ACGIH (TLV) 500 ppm, 1000 ppm STEL
isohexane (mixture of 2-methyl pentane & 3-methyl pentane)	(hexane isomer)
2-methyl pentane	(hexane isomer)
3-methyl pentane	(hexane isomer)
methyl cyclopentane	(hexane isomer)
neohexane (2,2 dimethyl cyclohexane)	(hexane isomer)
methyl cyclohexane (108-87-2)	500 ppm (new OSHA PEL was 400 ppm); [analogy to heptane -- narcosis]; ACGIH (TLV) 400 ppm
isopropyl alcohol (67-63-0)	400 ppm, 500 ppm STEL (mfg-strong acid process); [sensory irritation]; ACGIH (TLV) same
ethyl alcohol (64-17-5)	1000 ppm; [narcosis]; ACGIH (TLV) same

* PELs are from 29CFR1910.1000, Table 1; under the Hazard Communication Standard MSDSs are required for all of the compounds; all of the hydrocarbon solvents would be flammable liquids under the PSM Standard.

Table 2. Environmental (EPA) Regulations*

Chemical Name (CAS No.)	CAA			RCRA TCLP	RCRA Code Hazardous	EPCRA/SARA Title III				
						Sec. 302	Sec. 304			
	Title I (VOC)	Title III (HAP) (112r)				(EHS) TPQ	EHS RQ	CERLA RQ	Sec. 313	Sec. 311, 312
n-hexane (110-54-3	Yes	Yes	No	No	No	No	-	1+	Yes	Yes
n-heptane (142-82-5)	Yes	No	No	No	No	No	-	-	No	Yes
cyclohexane (110-82-7)	Yes	No	No	No	U056	No	-	1000	Yes	Yes
cyclopentane (287-92-3)	Yes	No	No	No	No	No	-	-	No	Yes
hexane isomers (none)	Yes	No	No	No	No	No	-	-	No	Yes
isohexane	[hexane isomer]									
2-methyl pentane	[hexane isomer]									
3-methyl pentane	[hexane isomer]									
methyl cyclopentane	[hexane isomer]									
neohexane	[hexane isomer]									
methyl cyclohexane (108-87-2)	Yes	No	No	No	No	No	-	-	No	Yes
isopropyl alcohol (67-63-0)	Yes	No	No	No	No	No	-	-	Yes	Yes
ethyl alcohol (64-17-5)	Yes	No	No	No	No	No	-	-	No	Yes

*From Title III Lists of Lists, U.S. EPA, EPA 560/4-92-011; 40 CFR 372; 40 CFR 52-99; 49 FR 4478 (Jan. 31, 1994); none are on the NTP or IARC list of carcinogens.

PROCESS SAFETY MANAGEMENT OF FLAMMABLE SOLVENTS

by
Dennis R. LaJeunesse
President
Operations Excellence, Inc.
Greensboro, North Carolina

Abstract

The vegetable oil extraction industry must comply with the OSHA Process Safety Management regulation. The inventory of hexane on site typically exceeds the threshold limit of 10,000 pounds for flammable solvents. Also, it is very likely that any replacement solvent for hexane will fall into the flammable category. Therefore, the industry should be directing efforts to achieve and maintain full compliance with Process Safety Management.

In addition, the vegetable oil extraction industry must address Title V of the Clean Air Act. A site must obtain a Federally enforceable permit due to hexane fugitive emissions and total VOC (Volatile Organic Compounds) emissions. Also, a MACT (Maximum Achievable Control Technology) standard will be set for the industry by EPA.

This presentation addresses the following specific items for the vegetable oil industry:

-The background and purpose of the regulations
-Threshold levels for compliance and methods to determine them
-Specific requirements of the regulations
-Timetables for compliance
-Specific recommendations to achieve compliance
-Related safety and environmental issues

Presentation

In the past several years OSHA (in the form of their Process Safety Management regulation, 29 CFR 1910.119) and EPA (in the form of their Air Permits program, 1990 Clean Air Act Amendments (CAAA), Title 5,) have imposed major requirements on the oilseed industry. As a result of their large on-site volume and utilization of hexane, essentially all solvent plants must comply.

Our intention is to provide a brief overview of OSHA's extensive Process Safety Management regulation and the Title V aspects of the 1990 Clean Air Act Amendments. We will cover the regulations' background, specific elements and comments on implementation. (Figure 1)

Process Safety Management

The background for Process Safety can be found in the 1980's and early 1990's. OSHA became concerned with large hazardous material related industrial accidents occurring throughout the world in locations such as Bopal, India (over 2000 fatalities), Channelview Pasadena, Texas (24 fatalities) and other localities. (Figures 2 and 3)

OSHA then drafted a regulation obtaining input from the chemical industry and other organizations. The result was 29 CFR 1919.119, Process Safety Management which became effective on May 26, 1992. With the full implementation of the regulation, OSHA saw the opportunity to achieve a major reduction in fires and explosions (by 80%), fatalities (down 260/year) and injuries/illnesses (down 1500/year). They also recognized that improvement in productivity and quality would occur. (Figure 4)

The regulation covers any process which involves one or more chemical above a specified threshold limit. Also, covered are those processes which involve a flammable liquid or gas in a quantity of 10,000 pounds or more. (Figure 5) .Hexane is a flammable liquid.

Before moving into the Process Safety Regulation itself, it is important to understand its relationship with "basic OSHA" which I will call Employee Safety. In examining the key elements (Figure 6) it important to note that many requirements for a successful program are common. For example both Process Safety and Employee Safety require Management Leadership, a system to Prevent accidents, and extensive use of Procedures and Training. The difference is that Process Safety is focusing on the Process (how a facility is operated) while Employee Safety is focusing on the individual employee (how they work). Another way to express this relationship is shown in the interacting circles in Figure 7. **Process Safety Management tells us in detail how we must run our hazardous material operations.**

What is Process Safety? Simply put, it is the establishment of procedures and systems for hazardous material processes to prevent fires, releases and explosions. (Figure 8) The operative words here are "procedures" and "systems" which you will see as we review the specifics of the regulation.

In the regulation itself, there are 14 specific paragraphs. (Figures 9 and 10) Reviewing these briefly,

-**Employee Involvement** - OSHA saw the lack of full employee involvement contributing to several of the major incidents.

-**Process Safety Information** - An extensive amount of information must be assembled for specific chemicals and processes and made available to the operating organization for use in training, procedures, hazards reviews.

-**Process Hazards Information** - These are structured reviews of each hazardous process by techniques such as HAZOP, WHAT IF. The regulation provides for a five year schedule.

-**Operations Procedures** - An organization must have procedures for all phases of operations such as startups, normal operations, emergencies.

-**Operator Training** - An organization must have a formal training, certification program in place.

-**Contractors** - They must know about the hazards on site and have their own safety program. Employers must keep a separate OSHA 200 log for contractors.

-**Pre-Start Up Safety Review** - An organization must conduct reviews for modified or new facilities.

-**Mechanical Integrity** - A comprehensive mechanical program must be established with

inspections, preventative maintenance, procedures, records and more.

-Safe Work Practices (Hot Work) - There must be a complete procedure in place.

-Management of Change - A system must be in place where all changes, except replacements in kind, must go through a review/approval system. This includes procedures, maintenance materials, raw materials and any other changes.

-Incident Investigation - A system must be in place to thoroughly investigate all incidents which could have resulted in a major incident. Full investigation followup is critical. Also, this is a good area for employee involvement.

-Emergency Response - A system to quickly respond to any incident is required. Many organizations have established an ER system under other OSHA, EPA regulations.

-Audits - Every three years, a complete audit of all Process Safety Management Elements must be completed with follow up corrective action.

-Trade Secrets - This paragraph protects proprietary information during investigations

The question often asked is "How difficult is it?" (Figure 11) The efforts varies among the elements. For example, the Hot Work item should be easy to implement while Operator Training is typically more involved. Also, the effort will depend on the organization's starting point. If there has been significant involvement is ISO 9000 or Total Quality Management, many of the required procedures and systems may be in place. In Figure 12, a comparison is made of the core elements between ISO 9000, Total Quality Management, OSHA's Process Safety Management, EPA's Risk Management Plan (under the Clear Air Act) and the Chemical Manufacturers Association's Responsible Care program are compared. The results show that core elements such as Management Responsibility, Procedures, Corrective Action and Training are common for all of these programs.

The 1990 Clean Air Act Amendments

The 1990 Clean Air Act Amendments (CAAA) were the first major revisions to Clean Air legislation since the 1977 amendments. The objectives of the regulation were to expand coverage to involve many more industrial and commercial facilities, establish an entirely new permitting program, substantially tighten requirements for pollution emission controls and drastically increase the potential civil and criminal liability for noncompliance for both individuals and corporation. (Figure 12)

The new air permit program will classify sources which exceed certain thresholds as large emitters. Specifically. any site with actual discharges in exceed of 100 tons/year of a criteria pollutant (SO_2, NOx, TSP, PM-10, CO and VOC) or 10 tons/year for one of 189 specific Hazardous Air Pollutant (HAP) or 25 tons/years for all HAP's will be a major source. (These thresholds are even lower in non-attainment areas as specified in the CAAA). Such a source will be required to pay a significant annual permit fee and a tonnage fee for all discharges. In additional, there will be significant monitoring and reporting requirements. (Figure 13)

The CAAA impact on the oilseed industry is in several areas. Again, the focus point is the solvent plant with its fugitive hexane losses. Hexane in a listed HAP in the CAAA. Therefore, given the high volume of annual hexane emissions, essentially all oilseed processing sites with a solvent plant will become major sources. (Figure 14)

Compliance Activities and Benefits

If there is a significant effort to achieve compliance with such demanding regulations, what are the expected benefits?. The short answer is "Plenty". Expanding on this, there should be considerable benefits consistent with OSHA's expectation to have incidents prevented. The industry wants to avoid problems such as experience by a soybean mill in 1994. A process upset occurred with a resulting major hexane release and explosions. The solvent plant was destroyed, there were four critical injuries and community claims of approximately $500,000 (Figure 15). The solvent plant is the heart of an oilseed plant. When a major incident results in a loss operations for any significant time period, the entire operation is shutdown. If it is the only plant for a smaller organization, a major incident can put the organization our of business.

Significant benefits can be found in productivity and quality improvements. **This in fact has been the experience of essentially all organizations who have fully implemented Process Safety Management.** The other benefits are penalty avoidance, better trained operators and reduced hexane losses. (Figure 16)

To assist in the implementation of Process Safety Management, the NCPA and Operation Excellence, Inc. jointly developed a Process Safety Management Implementation Manual for NCPA members. The manual must be tailored for each site, can immediately place an organization in compliance with a number the regulations requirements and will define the remaining outstanding items. Additional information is provided on the CAAA and several related safety issues. (Figure 17)

To ease the economic impact of the CAAA, oilseed producers should take steps to reduce hexane losses. Known losses account for only 40% of total losses. The remaining 60% of losses are fugitive in nature. Proper operation of the solvent plant and a systematic leak detection and repair program are required . (Figures 18 and 19)

In summary, Process Safety Management and the 1990 Clean Air Act are a major regulation and the effort to fully comply is a big job. You can't dance around it, they must be attacked head on with priority and resources. There is definitely an implementation cost, but at the same time, there will be considerable benefits. **Organizations who have partially or fully implemented Process Safety Management and Hexane loss reduction programs attest that the "projects" have provided a very good return.** Finally, integrate this effort into your culture, make it a part of the "way things are done". (Figure 20)

OVERVIEW OF OSHA 1910.119 AND TITLE V OF THE 1990 CLEAN AIR ACT

- INTRODUCTION AND BACKGROUND
- PROCESS SAFETY MANAGEMENT (PSM)
  - ELEMENTS
  - RELATIONSHIP TO OTHER OSHA REGULATIONS
  - EFFORT TO IMPLEMENT
  - PSM IMPLEMENTATION MANUAL
- 1990 CLEAN AIR ACT AMENDMENTS (CAAA)
  - ELEMENTS
  - AIR PERMITS
- COMPLIANCE ACTIVITIES AND BENEFITS
- SUMMARY

FIGURE 1 OPERATIONS EXCELLENCE, INC

PROCESS SAFETY MANAGEMENT
RECENT MAJOR INCIDENTS

IN THE WORLD

- 1970 FLIXBOROUGH (ENGLAND) INCIDENT WITH OVER 20 FATALITIES, TOTAL LOSS OF THE FACILITY
- 1974 SEVESO (ITALY) INCIDENT WITH MAJOR DIOXINE RELEASE RESULTING IN LARGE QUARENTINE/CLEANUP
- 1984 BHOPAL (INDIA) INCIDENT WITH MORE THAN 2000 FATALITIES

IN THE UNITED STATES

- 1989 PHILLIPS INCIDENT WITH 24 FATALITIES, 126 INJURIES
- 1990 ARCO CHEMICAL INCIDENT WITH 17 FATALITIES
- 1990 BASF INCIDENT WITH 2 DEATHS AND 41 INJURIES
- 1991 IMC INCIDENT WITH 8 DEATHS AND 128 INJURIES
- 1994 CENTRAL SOYA INCIDENT WITH 4 INJURIES, LOSS OF FACILITY

FIGURE 2 OPERATIONS EXCELLENCE, INC.

FIGURE 3

PROCESS SAFETY MANAGEMENT
MAJOR US INCIDENTS

OPERATIONS EXCELLENCE, INC

PROCESS SAFETY MANAGEMENT
PURPOSE OF STANDARD

PREVENT SITUATIONS AND CONDITIONS WHICH COULD PRODUCE UNWANTED RELEASES OF HAZARDOUS CHEMICALS RESULTING IN CATASTROPHIC EVENTS

EXPECTATIONS ARE:

- REDUCED FIRES AND EXPLOSIONS BY 80%
- PREVENT 260 OCCUPATIONAL FATALITIES ANNUALLY
- PREVENT 1500 INJURIES/ILLNESSES ANNUALLY

ADDITIONAL EXPECTED BENEFITS:

- INCREASE PRODUCTIVITY
- REDUCE DOWNTIME
- IMPROVE PRODUCT QUALITY

IMPLEMENTATION DATE: MAY 26, 1992 (MOST ELEMENTS)

FIGURE 4 OPERATIONS EXCELLENCE, INC.

PROCESS SAFETY MANAGEMENT
PROCESSES INVOLVED

PROCESSES COVERED INCLUDE:

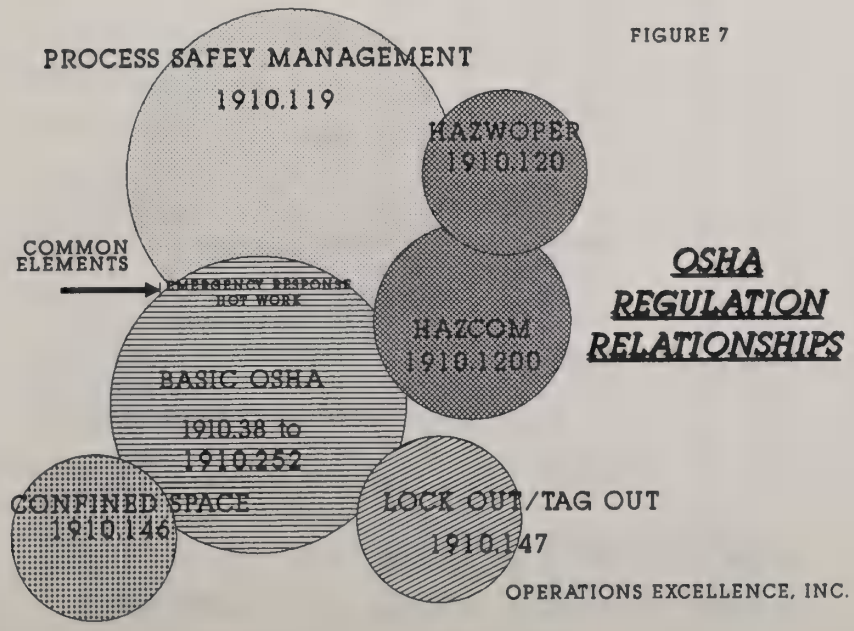
1. THOSE WHICH INVOLVE A CHEMICAL AT OR ABOVE THE THRESHOLD QUANTITIES LISTED IN APPENDIX A OF THE REGULATION (137 SPECIFIC SUBSTANCES)
2. THOSE WHICH INVOLVE A FLAMMABLE LIQUID OR GAS ON SITE, IN ONE LOCATION, IN A QUANTITY OF 10,000 LBS OR MORE (INCLUDES SOLVENTS SUCH AS HEXANE)

EXCEPTIONS TO ITEM 2 ARE:

A. HYDROCARBON FUELS USED SOLELY FOR WORKPLACE CONSUMPTION AS A FUEL
B. FLAMMABLE LIQUIDS STORED IN ATMOSPHERIC TANKS, OR TRANSFERRED WHICH ARE KEPT BELOW THEIR NORMAL BOILING POINT WITHOUT REFRIGERATION

FIGURE 6 OPERATIONS EXCELLENCE, INC.

FIGURE 7



OSHA REGULATION RELATIONSHIPS

OPERATIONS EXCELLENCE, INC.

PROCESS SAFETY MANAGEMENT
EMPLOYEE VS PROCESS

ITEM	BASIC OSHA	PROCESS SAFETY
FOCUS	EMPLOYEE	PROCESS
METHOD	PREVENTION	PREVENTION
WORST CASE SCENARIO	FATALITY	FATALITIES, SITE & COMMUNITY
METHODS	PROCEDURES TRAINING	PROCEDURES TRAINING
MANAGEMENT	LEADERSHIP	LEADERSHIP
EMPLOYEE	INVOLVEMENT	INVOLVEMENT

FIGURE 7 OPERATIONS EXCELLENCE INC

PROCESS SAFETY MANAGEMENT
WHAT IS IT?

THE ESTABLISHMENT OF PROCEDURES AND SYSTEMS FOR HAZARDOUS MATERIAL PROCESSES TO PREVENT FIRES, RELEASES AND EXPLOSIONS

FIGURE 8 OPERATIONS EXCELLENCE, INC.

PROCESS SAFETY MANAGEMENT

WHAT MUST BE DONE?

EMPLOYEE PARTICIPATION - POLICY, INVOLVEMENT

PROCESS SAFETY INFORMATION - HAVE ALL INFO FOR HAZARDS REVIEWS, EMPLOYEES USE

PROCESS HAZARDS INFORMATION - CONDUCT FORMAL REVIEWS

OPERATIONS PROCEDURES - WRITE THEM FOR ALL ROUTINE, NON-ROUTINE, EMERGENCY SITUATIONS

OPERATIONS TRAINING - TRAIN, TEST, CERTIFY

CONTRACTORS - INFORM AND QUALIFY ALL PERSONNEL

PRE START-UP SAFETY REVIEW - CONDUCT FOR ALL NEW, REVISED FACILITIES

FIGURE 9 OPERATIONS EXCELLENCE INC

PROCESS SAFETY MANAGEMENT

WHAT MUST BE DONE ? (CONT.)

MECHANICAL INTEGRITY - HAVE A STRUCTURED PREVENTATIVE, PREDICTIVE MAINTENANCE PROGRAM

SAFE WORK PRACTICES - HAVE A HOT WORK PROGRAM

MANAGEMENT OF CHANGE - A SYSTEM TO CONTROL ALL CHANGES IN TO THE PROCESS

INCIDENT INVESTIGATION - A SYSTEM TO LEARN FROM ALL INCIDENTS

EMERGENCY RESPONSE - A PLAN TO RESPONSE TO ANY EMERGENCY

SAFETY AUDITS - SELF CONDUCT EVERY 3 YEARS

TRADE SECRETS - PROTECTION FOR A COMPANY

FIGURE 10 OPERATIONS EXCELLENCE INC

PROCESS SAFETY MANAGEMENT

HOW DIFFICULT IS IT?

-THE EFFORT VARIES AMONG THE ELEMENTS

-ITEMS SUCH AS HOT WORK ARE STRAIGHTFORWARD

-WHILE ISSUES SUCH AS OPERATOR TRAINING AND CERTIFICATION ARE MORE INVOLVED

-THE EFFORT WILL ALSO DEPEND ON THE FACILITY'S STARTING POINT. FOR EXAMPLE, HAVING A GOOD SAFETY PROGRAM IN PLACE HELPS SIGNIFICANTLY

-SCHEDULE IS ALSO IMPORTANT. CONSISTENT WITH REGULATIONS, A MULTI MONTH APPROACH SHOULD BE TAKEN (CONTINUOUS IMPROVEMENT)

FIGURE 11 OPERATIONS EXCELLENCE, INC.

1990 CLEAN AIR ACT

OBJECTIVES

- EXPAND COVERAGE TO INVOLVE MANY MORE INDUSTRIAL AND COMMERCIAL FACILITIES
- ESTABLISH AN ENTIRELY NEW PERMITTING PROGRAM
- SUBSTANTIALLY TIGHTEN REQUIREMENTS FOR POLLUTION EMISSION CONTROLS
- DRASTICALLY INCREASE THE POTENTIAL CIVIL AND CRIMINAL LIABILITY FOR NONCOMPLIANCE FOR BOTH INDIVIDUALS AND CORPORATIONS

FIGURE 12 OPERATIONS EXCELLENCE, INC.

1990 CLEAN AIR ACT
PERMITS

- A SITE WILL REQUIRE A TITLE V (MAJOR SOURCE) PERMIT IF:

  EMISSIONS OF CRITERIA POLLUTANTS ARE OVER 100 TONS/YR (NOx, SOx, TSP, PM- 10, CO, VOC)

  - EMISSIONS OF 10 TONS/YR OF A SINGLE HAZARDOUS AIR POLLUTANT (HAP). THERE ARE 189 LISTED HAP'S INCLUDING HEXANE
  - EMISSIONS OF 25 TONS/YR OF ALL HAP'S COMBINED

- THE ABOVE THRESHOLDS ARE LOWER IN NON ATTAINMENT AREAS
- NEW PERMITS WITH INCREASED FEES (ANNUAL, TONNAGE), MONITORING AND REPORTING WILL BE REQUIRED

FIGURE 13 OPERATIONS EXCELLENCE, INC.

CLEAN AIR ACT
IMPACT ON OILSEED PRODUCERS

- SITES WILL REQUIRE TITLE V PERMITS DUE TO HEXANE LOSSES (>10 TONS/YEAR)
- ALSO, SITES ARE TYPICALLY ABOVE THE VOC THRESHOLD OF 100 TONS/YEAR
- AS A RESULT, SITES WILL PAY A FEE PER TON OF ALL REGULATED EMISSIONS (VOC, TSP, FUEL COMBUSTION PRODUCTS)
- TO MINIMIZE ECONOMIC IMPACT, STEPS SHOULD BE TAKEN TO REDUCE HEXANE LOSSES, OTHER EMISSIONS
- BY ACTING NOW, OILSEED PRODUCERS CAN POSITIVELY IMPACT THE MACT TO BE IMPOSED BY EPA BY 2000

FIGURE 14 OPERATIONS EXCELLENCE INC

HEXANE INCIDENT
OILSEED PLANT EXPLOSION

- A MIDWEST SOYBEAN PLANT HAD A MAJOR INCIDENT IN THE SUMMER OF 1994
- HIGH PRESSURE LED TO A RUPTURE. THE RESULTING RELEASE OF HEXANE CAUSED AN EXPLOSION/FIRE
- THE INCIDENT WAS COMPLICATED BY A SECONDARY EXPLOSION (DUST) AND A STILL NIGHT. OIL TANKS CAUGHT FIRE
- FOUR INDIVIDUALS WERE CRITICALLY INJURED INCLUDING A MOTORIST WHOSE CAR IGNITED THE VAPOR CLOUD
- EXTRACTION WAS EXTENSIVELY DAMAGED AND WELL AS OTHER PARTS OF THE FACILITY
- CLAIMS SETTLEMENTS ARE OVER $250,000

FIGURE 15 OPERATIONS EXCELLENCE, INC.

PROCESS SAFETY MANAGEMENT
WHAT ARE THE BENEFITS?

✓ PREVENTION OF INCIDENTS
-MINOR OUTAGES WHICH LIMIT THROUGHPUT
-MAJOR INCIDENT WHICH SHUT DOWN OPERATIONS

✓ SUPPORTS OSHA COMPLIANCE AND FINE AVOIDANCE

✓ BETTER TRAINED OPERATORS AND IMPROVED ASSIMILATION OF NEW EMPLOYEES

✓ IMPROVED KNOWLEDGE OF OPERATIONS
-IMPROVED THROUGHPUTS AND RECOVERY
-REDUCED HEXANE LOSSES

FIGURE 16 OPERATIONS EXCELLENCE, INC

PROCESS SAFETY MANAGEMENT
NCPA IMPLEMENTATION MANUAL

- ✓ DEVELOPED SPECIFICALLY FOR COTTONSEED OIL MILLS
- ✓ MUST BE TAILORED FOR EACH SPECIFIC SITE
- ✓ PROVIDES INFORMATION TO IMMEDIATELY MEET MANY BUT NOT ALL OF THE REGULATIONS REQUIREMENTS
- ✓ PLACES ORGANIZATION ON THE PATH TO COMPLIANCE
- ✓ A SITE SPECIFIC IMPLEMENTATION SCHEDULE MUST BE DEVELOPED AND FOLLOWED TO ACHIEVE COMPLIANCE
- ✓ ADDITIONAL INFORMATION IS PROVIDED ON
  - -THE CLEAN AIR ACT'S IMPACT
  - -RELATED SAFETY ISSUES

FIGURE 17 OPERATIONS EXCELLENCE, INC.

HEXANE LOSS MANAGEMENT
REDUCTION EFFORTS

- KNOWN LOSSES OCCURRING IN THESE AREAS GENERALLY ACCOUNT FOR 40% OR LESS OF TOTAL LOSSES
  - -MEAL PRODUCT
  - -CERTAIN AIR AND WATER STREAMS
- ALL OTHER LOSSES ARE FUGITIVE IN NATURE RESULTING FROM SOURCES SUCH AS PUMPS, PIPING SYSTEMS, TANKS, ETC.
- TO MINIMIZE LOSSES, A TWO-FOLD APPROACH IS REQUIRED
  - -PROPER OPERATION OF EXTRACTION PROCESS
  - -A SYSTEMATIC LEAK DETECTION PROGRAM

FIGURE 18 OPERATIONS EXCELLENCE, INC.

COST OF HEXANE LOSSES
MATERIAL AND FEES

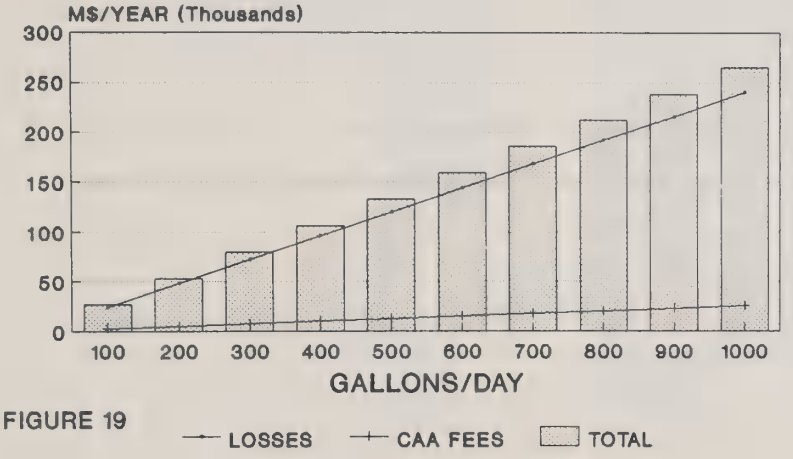


FIGURE 19

HEXANE-$.80/GAL,CAA FEE-$25/TON, 300 D

PSM AND CAA
CONCLUSIONS

- THEY ARE SIGNIFICANT REGULATIONS THAT FOCUS ON THE HEXANE EXTRACTION PROCESS
- THEY MUST BE ADDRESSED ON A PRIORITY BASIS WITH APPROPRIATE RESOURCES ASSIGNED
- FOR PSM, ALL MAJOR ELEMENTS SHOULD BE IN PLACE OR ON A PATH TOWARDS COMPLIANCE
- FOR BOTH PSM AND THE CAA, UNDERSTANDING AND MANAGING THE HEXANE EXTRACTION PROCESS ARE KEYS
- INTEGRATE INTO YOUR CULTURE BUILDING ON CURRENT PROGRAMS, EMPHASIZING PREVENTION

FIGURE 20 OPERATIONS EXCELLENCE, INC.

MINIMIZING SOLVENT LOSS IN SOYBEAN SOLVENT EXTRACTION PLANTS

by

Timothy G. Kemper
Director of Engineering
Oilseed Divisiion
French Oil Mill Machinery Company
Piqua, Ohio, U.S.A.

As the next century approaches, industry is fully engaged in quality, knowing that continuous improvement is an essential strategy for future prosperity. Quality also applies to our environment. We must continuously improve our processes to reduce the negative impact imparted on the environment.

For the oilseed processing industry, one of the negative impacts imparted on the environment is the unrecovered solvent from the vegetable oil extraction process. The solvent most commonly used in this process is hexane, which has been identified as a hazardous air pollutant by recent environmental regulations. The oilseed processing industry must strive to continuously improve solvent recovery to improve the quality of the environment we live in.

In the early years of solvent extraction of vegetable oil from oilseeds, it was considered "good" solvent recovery in a soybean solvent extraction plant to recover 99.72 percent of the solvent pumped into the extractor. This rate of recovery appeared both respectable and economically feasible. In other terms, approximately 1.0 gallon of solvent was lost for every ton of soybeans processed.

In the 1970's, with the advent of larger plants and new technology for scrubbing solvent from the exiting process air, what was considered "good" solvent recovery in a soybean solvent extraction plant improved to 99.86 percent of the solvent pumped into the extractor. In other terms, the solvent loss was reduced to approximately 0.5 gallons of solvent per ton of soybeans processed.

This remained what was considered "good" solvent recovery until the 1980's and 1990's when plants installed improved desolventizer toasters utilizing fully countercurrent stripping steam. Presently, most processors consider "good" solvent recovery in soybean solvent extraction plants to be 99.92 percent of the solvent pumped into the extractor, resulting in a loss of approximately 0.3 gallons of solvent per ton of soybeans processed.

To maximize solvent recovery in a modern soybean solvent extraction plant the following technology must be in place:

A. Desolventizer Toaster
   - fully countercurrent, evenly distributed live steam flow
   - superheat in steam supply (350°F @ 20 psig)
   - adequate discharge meal temperature (220°F or higher)
   - adequate residence time (20 minutes or more)

B. Mineral Oil System
   - low entering vapor temperature (100°F or lower)
   - sufficient scrubbing contact area (see max. design vapor flow)
   - sufficient stripping contact area (see max. design vapor flow)
   - sufficient mineral oil flow (see min. design oil flow)
   - low enough cool mineral oil temperature (95°F or lower)
   - high enough hot mineral oil temperature (220°F or higher)
   - fully countercurrent, evenly distributed vapor to oil flow
   - superheat in steam supply (350°F @ 0 psig)
   - good quality mineral oil

C. Final Oil Stripper
   - adequate oil concentration in (97% oil or higher)
   - adequate oil temperature in (220°F or higher)
   - fully countercurrent, evenly distributed live steam flow
   - superheat in steam supply (350°F @ 0 psig)
   - adequate stripping contact area (see max. design oil flow)
   - adequate vacuum level (24 inches Hg or higher at sea level)

D. Waste Water Evaporator
   - adequate water temperature (185°F or higher)
   - adequate residence time (20 minutes)

With properly sized, latest technology equipment in place under consistent operating conditions, the following solvent loss assumptions can be made for a soybean solvent extraction plant:

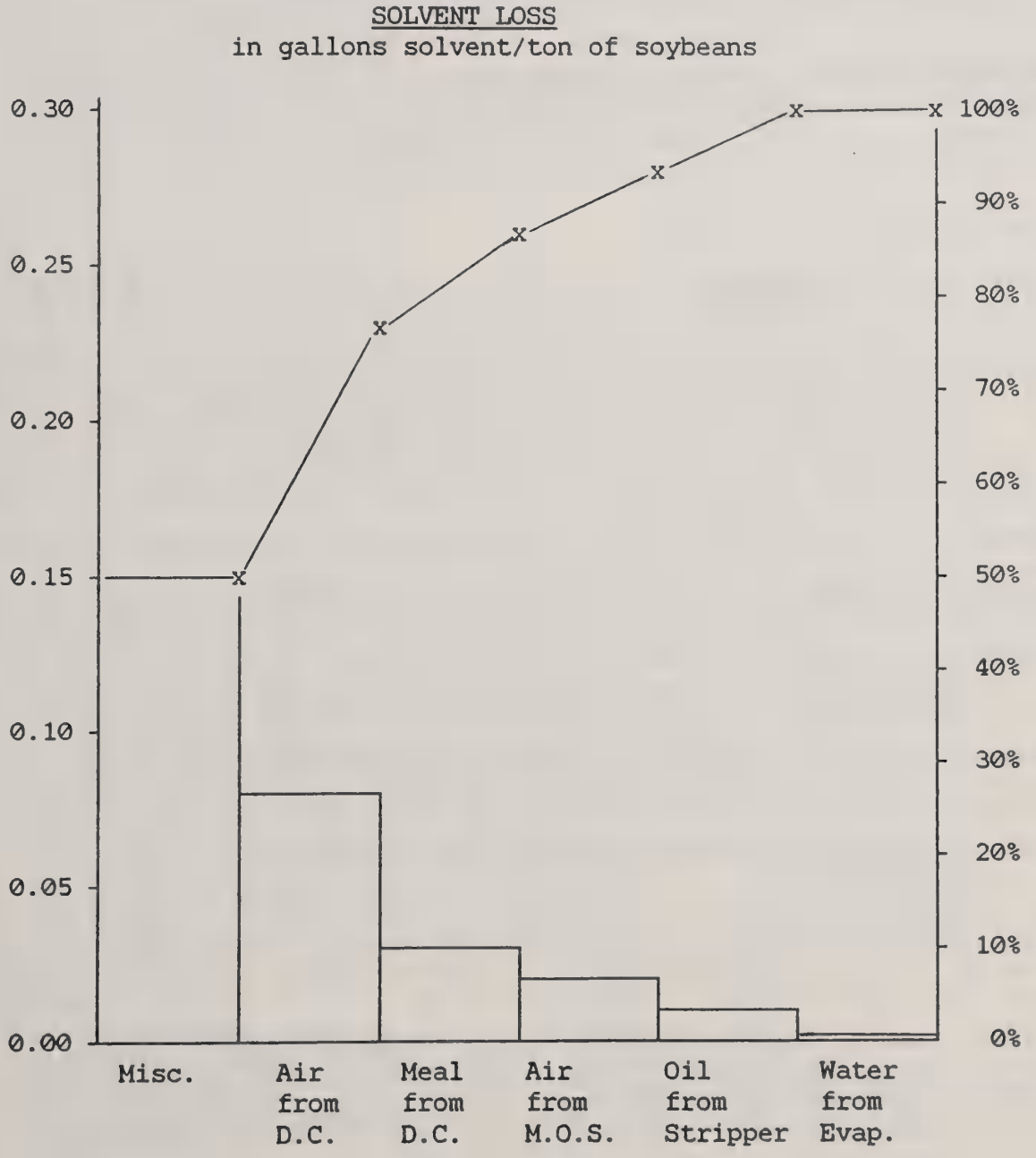
solvent loss in meal from desolventizer toaster:	400 ppm
solvent loss in meal from dryer cooler:	100 ppm
solvent loss in air from mineral oil system:	30% LEL
solvent loss in oil from final oil stripper:	200 ppm
solvent loss in water from waste water evaporator:	10 ppm

These solvent losses when applied to the mass balance of a soybean solvent extraction plant provide the following solvent loss analysis:

*solvent loss in meal from dryer cooler:	0.028 gallons/ton
*solvent loss in air from meal dryer cooler:	0.083 gallons/ton
solvent loss in air from mineral oil system:	0.021 gallons/ton
solvent loss in oil from final oil stripper:	0.013 gallons/ton
solvent loss in water from waste water evaporator:	0.002 gallons/ton
Accountable solvent loss:	0.147 gallons/ton

Assuming good solvent loss is 0.300 gallons per ton of soybeans, and the accountable solvent loss with properly sized, latest technology equipment operating consistently is 0.147 gallons per ton of soybeans, then the remaining "miscellenous" solvent loss is 0.153 gallons per ton of soybeans.

In order to develop a plan to further improve solvent recovery, and thus minimize solvent loss, we can now apply quality tools and techniques. To begin this process, a Pareto diagram can be effectively used to illustrate the sources of solvent loss and their relative magnitude:



From the Pareto diagram, the primary source of solvent loss in a soybean solvent extraction plant is miscellaneous loss, assuming 0.300 gallons of solvent loss per ton of soybeans and properly sized, latest technology equipment operating consistently. To better identify this miscellaneous solvent loss it can be broken down into three categories:

A. Excess loss

B. Fugitive loss

C. Purging loss

The relative magnitude of each of these loss categories is difficult to measure, but we know that together, this miscellaneous loss is the most significant source of solvent loss remaining, and the source that must be managed through a quality process in order to further improve solvent recovery, and thus minimize solvent loss. A general definition, analysis, and action plan for the three catagories of miscellaneous solvent loss follows:

Excess Loss

Excess loss is the amount of additional loss through air from the meal dryer cooler, through meal from the meal dryer cooler, through air from the mineral oil system, through oil from the final oil stripper, and through water from the waste water evaporator, as a result of inconsistent operation, or a lack of properly sized, latest technology equipment. The excess loss due to inconsistent operation occurs during the period starting when the input conditions change and ending when the input conditions change back to normal, or during the period starting when the input conditions change and ending when steady state is achieved after the operating parameters have been changed.

Examples of excess solvent loss are many. One example is that flake thickness is reduced from 0.014 inches to 0.012 inches. This results in a reduction in extractor drainage rate, which in turn increases the solvent flow rate to the desolventizer toaster. There is a time period in which the solvent flow rate to the desolventizer toaster is increased before temperatures decrease and cause the feedback steam flow controller to add additional steam. During this period of time, the meal discharge temperature is lower than normal and the amount of solvent exiting the desolventizer toaster may increase dramatically. This subsequently increases the amount of solvent loss through the air from the meal dryer cooler.

Other examples of excess solvent loss can be more subtle. Solvent is pumped into the work tank from storage. The increased work tank level reduces the total pump head slightly, and therefore, the solvent pump flow rate increases slightly. More solvent is pumped into the extractor, and thus more solvent goes out with the full miscella. This results in lower temperatures and concentrations into the final oil stripper, until the feedback control valve on the second stage evaporator reacts to the change in temperature. During

this time period, the amount of solvent in the oil exiting the final oil stripper may increase substantially.

The actions that can be taken to minimize excess solvent loss are:

1. Install properly sized, latest technology equipment.

2. Improve the consistency of the input product to the solvent extraction plant. This includes rate, moisture, flake thickness, hull content and fines content. It is important to note that this is the responsibility of the soybean receiving and preparation plants, whose internal customer is the soybean solvent extraction plant.

3. Improve the consistency of parameters within the solvent extraction plant, particularly during shift changes. This includes levels, pressures, temperatures and flows.

4. Install automatic control mechanisms which quickly react to operational inconsistencies and respond by changing operating parameters. It is important to note that these controls must be properly applied to prevent large swings in operating parameters which can cause further inconsistency and excess solvent loss.

Fugitive Loss

Fugitive loss is the amount of solvent loss from the process equipment through flanges, doors, packing glands, pump seals, valve stems, sight glasses, etc. This loss occurs when the pressure inside of vessels is greater than atmospheric pressure, causing solvent vapor inside the vessel to leak out through any orifice.

Fugitive solvent loss is not proportional to rate, therefore, larger plants can be expected to have lower fugitive solvent loss than an average sized plant and smaller plants can be expected to have higher fugitive solvent loss than an average sized plant, on a gallons per ton basis.

The actions that can be taken to minimize fugitive solvent loss are:

1. Pressure test all equipment and piping with compressed air to insure the system is free of leaks prior to starting operation.

2. Maintain process equipment under a slight vacuum where possible. This will allow air to leak in, rather than allowing solvent vapor to leak out. It is important to note that too much vacuum will cause excess air to pull in and overload the mineral oil system, which will cause excess solvent loss.

3. Use specially designed seals on any process equipment normally operating under pressure, where solvent is present. Examples of process equipment normally operating under pressure where solvent is present are solvent and miscella pump seals and valve stems, and lower sections of the Desolventizer Toaster. Double pump seals, special valve stem packings, and heavy duty manway doors with graphite packing are examples of specially designed seals.

Purging loss

Purging loss is the amount of solvent loss from the process equipment resulting from freeing the process equipment of solvent vapor for inspection or maintenance. This loss occurs as a result of opening up the process equipment, and as a result of using purge fans to pull air through the process equipment.

During normal operation, purging loss does not exist. Purging loss only exists when the plant is shut down. As a result, the solvent loss as a result of purging can not be quantified in terms of gallons of solvent loss per ton of soybeans processed on a direct basis, as with the other categories of solvent loss. Therefore, purging loss is typically added to total solvent loss on an annual basis, and then factored out in terms of gallons of solvent loss per ton of soybeans processed. When comparing solvent loss from facility to facility, it is important to note whether or not purging loss has been taken into consideration.

The actions that can be taken to minimize purging solvent loss are:

1. Improve equipment reliability through design improvements, and through thorough preventative maintenance processes. This will reduce the frequency for which maintenance and inspection are required, thus reducing the frequency of vapor freeing and its related purging solvent loss.

2. Allow the normal vapor recovery system to run as long as possible prior to opening up the process equipment. This will recover the majority of the solvent prior to vapor freeing, thus reducing purging solvent loss.

3. Discharge the purge fan through a condenser to recover as much of the solvent vapor as possible, thus reducing purging solvent loss.

In summary, with a good solvent loss of 0.300 gallons per ton of soybeans, and properly sized, latest technology equipment operating consistently, the primary source of solvent loss is the collective miscellaneous loss from excess loss, fugitive loss, and purging loss. For the oilseed processing industry to continuously improve solvent recovery, and thus minimize solvent loss, there must be a good quality process in place. A quality process for managing solvent loss is to define each category of loss, collect data and analyze the relative magnitude of each category of loss, select the most significant category of loss, plan actions to minimize this category of loss, execute those actions, evaluate their effect, implement the successful actions and continuously improve by repeating this quality process. Facilities with good quality processes in place will lead the industry in solvent recovery, and minimizing solvent loss.

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* Soybean is the easiest material to desolventize, and as a result, solvent loss in other oilseeds will be greater in the areas of air from the meal dryer cooler, and in meal from the meal dryer cooler.

ALTERNATE HYDROCARBON SOLVENTS - PLANT TRIALS

by

P. J. Wan, R. J. Hron, Sr., M. Dowd, S. Kuk and E. J. Conkerton
Southern Regional Research Center
Agricultural Research Service
United States Department of Agriculture
1100 Robert E. Lee Boulevard
New Orleans, Louisiana 70124

Phone:504-286-4450; FAX:504-286-4419

SUMMARY

Hexane has been used to extract oil from cottonseed for decades and is still the solvent of choice for the edible oil industry. Due to the pending 1990 Clean Air Act and potential health risk, the edible oil extraction industry urgently needs alternate hydrocarbon solvents to replace hexane. Based on lab scale extraction tests, two hydrocarbon solvents: heptane and isohexane were recommended as potential replacements for hexane. A cottonseed processing mill with 300 tons/day capacity agreed to test both solvents with their expander-solvent process. Extraction efficiency of isohexane and heptane, judged by extraction time and residual oil in meal, refined and bleached color of miscella refined oil, and solvent loss was comparable to that of hexane. However, processing with the lower boiling isohexane was noticeably easier than with the higher boiling heptane. Using isohexane the daily throughput increased more than 20% and natural gas consumption decreased more than 40% as compared to hexane.

INTRODUCTION

Local governments will soon regulate the emission of volatile organic compounds (VOC's) based on the 1990 Clean Air Act (1, 2). Hexane, the extraction solvent for cottonseed and many other oilseeds, will be regulated as both a Criteria and a Hazardous Air Pollutant. Criteria Pollutants include particulate matter, ozone or its precursor, i.e., volatile organic compounds (VOC's). There are 189 toxic chemicals cited as Hazardous Air Pollutants (HAP's) (2); this list includes n-hexane which is the main component of commercial hexane. The emission limit under Criteria Pollutants is 100 tons per year (tpy) per plant. A much lower limit, 10 tpy, was set for HAP's. Exceeding either limit will require a Federal Operating Permit, at a fee of $25 per annual ton of hexane consumed (1).

While the industry continues its effort to reduce the loss of hexane, laboratory research of alternate hydrocarbon solvents with less health risk led to a study of two candidate solvents: heptane and isohexane (3). Performance of both solvents as well as hexane were conducted in a cottonseed processing facility with a capacity of 300 tons/day in March, 1994. Results of these trials are reported.

MATERIALS AND METHODS

Seven thousand gallons of heptane and of isohexane were supplied by Phillips Petroleum Company (Bartlesville, OK). Chemical compositions and some selected physical properties for hexane, heptane and isohexane as provided by the supplier and are listed in Tables 1 and 2, respectively.

Both candidate solvents were evaluated in a 300 tons/ day cottonseed expander-solvent extraction mill equipped with miscella refining capability. A flow diagram describing the operation is shown in Figure 1. When isohexane was used, an additional cooling step, COOLER II, was added to reduce the temperature of collets below 100°F before entering the extractor. Operating conditions were recorded for the two candidate solvents as well as for hexane.

Residual oil content of extracted collets and meals was monitored at least once every eight hours by the plant laboratory. Free fatty acid, gossypol and phosphorus content in the extracted crude oils were determined at the Southern Regional Research Center (SRRC) and a commercial lab according to AOCS Official Methods Ca 5a-40, Ca 13-56 and Ca 12b-92 (5), respectively. Refined oil was bleached in a commercial lab and the color of refined and bleached oil was measured according to AOCS Method Cc 13b-45 (5). Miscella concentration expressed as percent oil by weight in the miscella (mixture of oil and solvent) was estimated by a density method used at the mill.

RESULTS AND DISCUSSION

Some of the extraction conditions and results for hexane, isohexane and heptane are shown in Table 3. When the residence time of collets in the extractor, full miscella concentration and residual oil in the extracted collets were compared, the candidate solvents showed an extraction efficiency comparable to that of hexane. Results obtained from a separate week-long plant trial showed that the residual oil in extracted collets were 1.00 ± 0.17% for isohexane (mean ± standard deviation of 16 samples) and 0.87 ± 0.06% for hexane (20 samples). These additional plant results confirmed the lab scale observatioin (3) that isohexane can extract 97%+ oil out of cottonseed and hexane is slightly more efficient

than isohexane under the extraction conditions described in Table 3. Only occasional, slightly higher pressure was noted in the extractor for isohexane which was believed to be caused by insufficient cooling of the collets prior to extraction. High energy demand to recover heptane from marc (extracted collets) slowed down the entire process. Residence time of collets in the extractor, in some cases, was extended to more than 100 minutes as opposed to a normal residence time of 46 minutes. This extended extraction time did not affect the oil quality (Table 4).

Plant refinery records and results for all three solvents, Table 4, demonstrated that oils derived from isohexane and heptane were bleachable to a color similar to that of hexane. The cloudy appearance observed in refined isohexane miscella was of initial concern and was believed to be caused by higher than optimum operating temperatures for the miscella refining process. However, the refined oil still met the bleachable color standard for Prime Bleachable Summer Yellow (PBSY), < 2.5 red (6). Free fatty acid contents in miscella before refining were comparable for all three solvents.

Desolventization of isohexane extracted collets operated smoothly. Due to the lower boiling range of isohexane, throughput rate of the Desolventizer-Toaster (D/T) was 10-20% higher than that of hexane. The higher boiling heptane caused a 20-30% reduction in daily throughput (Table 5). Therefore, the experiment with heptane was stopped after three days of continuous operation. During the operating period, the solvent loss of heptane was 12% higher than that of hexane. Losses of isohexane on the other hand were about 86.8 to 97.4% of hexane's annualized average loss. It should be noted, however, due to the short duration of the plant test, the solvent loss data may not reflect the true differences between the candidate solvents and hexane.

Two-day samples of miscella before refining (MBR) and miscella refined oil (MRO) were obtained from hexane, isohexane and heptane extractions. MBR samples were desolventized in a rotary vacuum evaporator at SRRC. Compositional analysis and color readings of oils derived from MBR and MRO were done and their mean values are presented in Table 6. Oils of MBR samples derived from heptane contained less gossypol and more phosphorus than those derived from hexane and isohexane which confirmed the bench extraction results (3). This implied that heptane has greater solubility of phospholipids and less affinity toward gossypol than the other two hydrocarbon solvents. Color of desolventized MBR, or crude, oils varied proportionally to the amount of gossypol present. All MRO samples were desolventized in the mill operation and were sufficiently low in moisture and volatiles, phosphorus content and light in color. MRO samples derived from isohexane miscella contained more than 20 ppm phosphorus which is significantly higher than that from hexane or heptane. This problem could be caused by refining at higher than optimum temperatures and should be verified

and corrected during a proposed extended run. All MRO oils produced from the three solvents were bleached by a commercial lab to a color less than the required 2.5 red for PBSY which confirmed the plant results shown in Table 4. Composition of meals produced from all three solvents, Table 7, indicated some consistency. The differences in protein contents were due to variation in the amount of hulls present in dehulled meat fractions.

From the overall performance of heptane and isohexane as extracting solvents and the quality of meal and oil produced by these two candidate solvents, it appears that isohexane can be used to replace hexane with minimum retrofit. Heptane, however, requires greater D/T capacity to maintain the same tonnage throughput found with hexane. This might not be economical for most edible oil extraction operations. However, the high boiling point of heptane allows it to be operated at a broad temperature range, from ambient to 80°C (176°F) which could be advantageous in extracting substances with melting points higher than vegetable oils. Isohexane boils above 55°C (131°F) and therefore has a rather narrow operating temperature range, between ambient and the 45°C extraction temperature. This lower extraction temperature may also be one cause for the slightly lower extraction efficiency of isohexane as indicated by slightly higher residual oil in spent collets (Table 3) than hexane, which confirmed the bench scale extraction results (3). Overcoming the slightly reduced extraction efficiency of isohexane is believed achievable by some process adjustments.

The advantage of using isohexane, aside from its lower health risk than hexane (7), is probably the significantly lower energy requirement for its recovery. Table 8 shows an example of the energy savings based on natural gas consumption for steam generation for a one-week period. Isohexane was found to reduce the natural gas consumption by more than 40% over that of hexane as opposed to a theoretical estimate of less than 3% savings (3). Rapid removal or stripping of isohexane should also provide the basis for a dramatic increase in throughput which was observed during this plant trial. Under present economic environment and regulatory concerns, isohexane becomes the obvious choice to replace hexane for cottonseed extraction. The only hurdle left is the supply and price of isohexane.

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Figure Legend

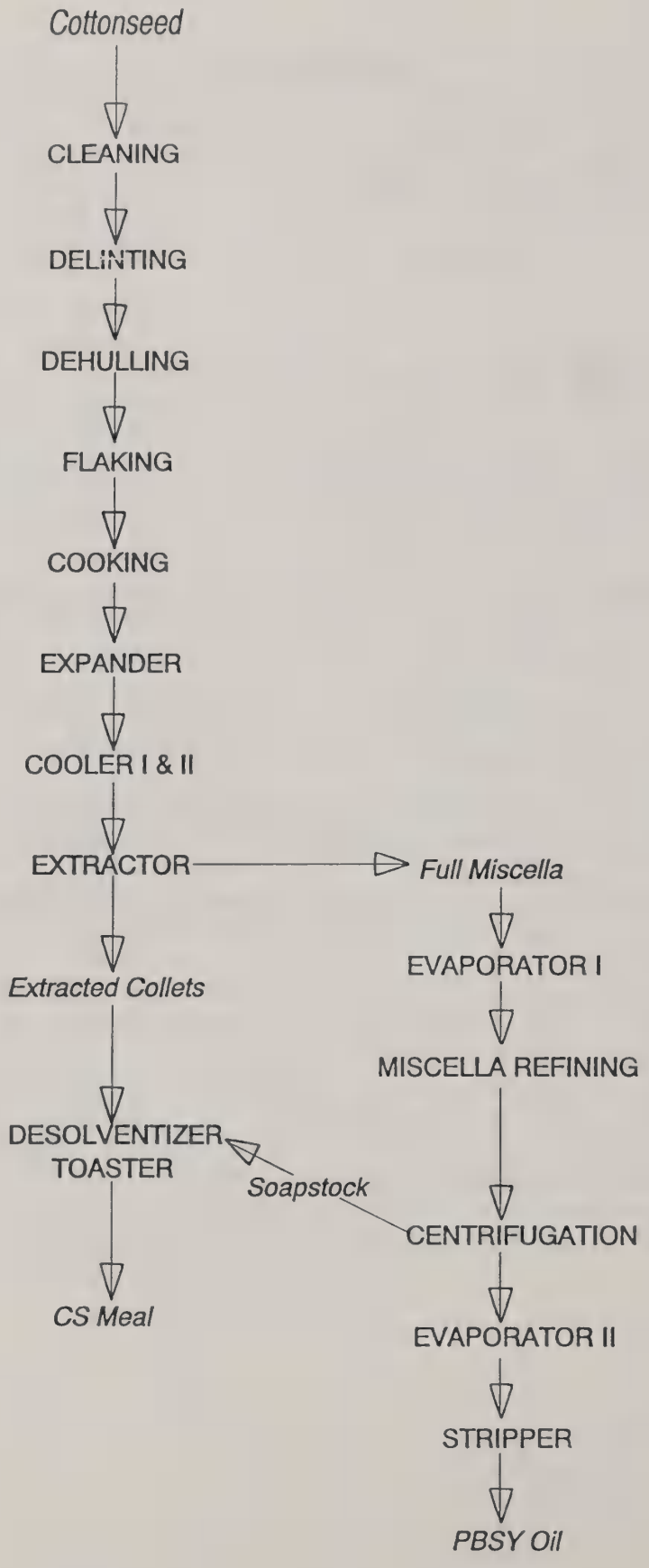


FIG. 1. Flow Diagram of Expander Solvent Extraction of Cottonseed

TABLE 1

Composition of solvents used in plant trials[a]

Component	Hexane Lv%[b]	Heptane Wt%	Isohexane Wt%
Hydrocarbon with 5-C or less			0.9
2,2-Dimethylbutane		0.07	14
2,3-Dimethylbutane		0.08	15.9
2-Methylpentane	0.24	0.22	46.3
3-Methylpentane	3.95	0.1	20.1
n-Hexane	86.18	0.02	2.6
Methylcyclopentane	9.62		0.2
Cyclopentane derivatives		7.09	
Cyclohexane derivatives		0.83	
2-Methylhexane		21.55	
3-Methylhexane		28.21	
n-Heptane		23.63	
Other isoheptanes		12.58	
Toluene		3.54	
Other unsaturated hydrocarbons		2.08	

[a] Data were provided by the supplier.
[b] Lv% = Liquid volume %

TABLE 2

Physical Properties of Selected Hydrocarbon Solvents

Properties	Types of Solvent			
	Hexane	Heptane	Isohexane	Neohexane
Boiling Range °C (°F)	67 - 69 (152 - 156)	91 - 100 (195 - 212)	55 - 61 (131 - 142)	49 - 51 (121 - 124)
Heat of Vaporization cal/g (Btu/lb)	80 (143.9)	75.6 (136)	77 (139)	72.9 (131.2)
Liq. Sp. Heat cal/g/C	0.533	0.528	0.52	0.516
Vap. Sp. Heat cal/g/C	0.386	0.385	0.39	0.382
Specific Gr. (16 C/60 F)	0.679	0.694	0.66	0.655

TABLE 3

EXTRACTION PERFORMANCE[a]

Operation Condition	Hexane	Isohexan	Heptane
Collet Temp to Extractor, F	150	119.8	158.6
Extractor Temp., F	146.3	136.2	150.6
Residence Time in Extractor, min	45	46.2	91.4
Concentration of Full Miscella, %	29.5	31.1	29.9
Residual Oil in Extracted Collets,%	0.93	1.00	0.66
Average Moisture, %	11.30	10.90	10.50
Desolventizer Toaster Temp., Range F,	140-210	130-225	154-225

[a] All values were supplied by the plant.

TABLE 4

Refinery Operation Conditions and Results[a]

Operation Condition	Hexane	Isohexane	Heptane
Second Stage Evaporator Temp, F	249.4	272.3	303.1
Stripper - Vacuum, inches	23.5	21.2	24.2
Stripper-Bottom Temp, F	251.9	253.1	274.4
Miscella Concentration before Ref, %	67	67	66.6
Miscella Free Fatty Acid, %	1.59	1.68	1.54
Miscella Refined Oil Color, Red	4	4.2	4.1
Bleached Color, Red	1.6	1.5	1.6

[a] All values were supplied by the plant.

TABLE 5 DAILY THROUGHPUT RATE AND SOLVENT CONSUMPTION

Operation Condition	Hexane	Isohexane	Heptane
Throughput Rate, tons CS/Day	300	320 - 366	282
Range, %	100	107 - 122	67 - 77
Solvent Consumption, as % of Hexane	100[a]	97.4[b]	112.6[c]

[a] Annualized average solvent consumption.
[b] Weekly average solvent consumption.
[c] Average of 3-day operation.

TABLE 6

Composition of Meals[a]

Composition	Hexane	Isohexane	Heptane
Moisture, %	10.66	9.69	8.18
Oil, %	2.38	2.31	2.67
Protein, % [b]	41.9	44.43	39.75

[a] Average of two or more replicate samples.
[b] Protein % = (Nitrogen %) x 6.25

TABLE 7

Composition and Color of Oils from Miscella Before Refining (MBR) and Miscella Refined Oil (MRO)[a]

Analysis	Hexane		Isohexane		Heptane	
	MBR	MRO	MBR	MRO	MBR	MRO
Moist & Volatile, %	0.35	0.04	0.85	0.05	1.5	0.04
Free Fatty Acid, %	1.95		2.4		1.75	
Gossypol, %	0.738		0.697		0.466	
Phosphorus, ppm	737	3.00	707	23.50	778	3.50
Color, Red[b]	12.5	3.85	10.3	4.95	8.8	3.70
Bleahed Color, Red		1.30		1.90		1.15

[a] All values are averages of duplicate samples.
[b] Color of oil derived from MBR was read in a 5 mm cell and color of MRO was read in a 133.35 mm (5.25 in) cell using an automated Colourscan.

TABLE 8

Natural Gas Usage for Steam Generation

Solvent	Tons CS Per Week	MCF Gas[a] Per Week	Cu Ft Gas Per Ton CS	% Savings Per Ton CS	% Savings Per Week
Isohexane	2064	202.9	98.30	38.27	42.76
Hexane	2226	354.5	159.25	Control	Control

[a] MCF = 1000 cubic feet.

SUPPLY AND COST OF ALTERNATIVE HYDROCARBON SOLVENTS

by

R. W. Emerson
North America Sales Manager
Specialty Chemicals
Phillips Chemical Company, a division of Phillips Petroleum Co.
Bartlesville, Oklahoma

The papers that have already been presented provided information regarding the comparative health, environmental and regulatory concerns of normal hexane and other hydrocarbon solvents. In addition, Dr. Wan has presented information obtained during a plant trial in which these alternate solvents were evaluated. The purpose of this paper is to provide you with our understanding of (a) the current relative price differentials between n-hexane, n-heptane and isohexane, (b) how these price differentials are likely to change in the future and (c) the current and anticipated availability of these products.

Exhibit A shows the current relative market prices of the three alternative solvents. n-Hexane is shown here as the benchmark with a value of 100%. As you can see, n-hexane and n-heptane are priced at relatively the same level, (heptane costs only about 5% more than hexane). Isohexane, on the other hand, sells for about 35% more than n-hexane.

Why do the current price gaps exist? One reason is the size of the markets for these solvents. Exhibit B provides an estimate of the relative market size of these products in North America. Again, n-hexane is used as the benchmark at 100%. As you can see, demand for both n-heptane and isohexane is much smaller than it is for n-hexane. In fact the isohexane market is currently only about 1% as large as the hexane market. So part of the reason for the price gap between these products can be attributed to the relative size of their markets. If demand for n-heptane and isohexane grows, economies of scale will lower production costs. This in turn should result in smaller price differentials between them and n-hexane. The rate at which demand for these products grows will determine the rate at which the price differentials decay.

Although market size is one reason for the current price gaps, in the case of isohexane, market size is not the only reason. Part of the price difference results from the way isohexane is made. Exhibit C shows a simplified process flow diagram for isohexane. This flow diagram starts at the well head with natural gas liquids and crude oil. These feed streams are processed and separated into many products, including small quantities of naturally occurring isohexane and large quantities of n-hexane. Much of the n-hexane is captured at this point and sold as a commercial solvent. The rest of the n-hexane and the isohexane are processed further in a hexane isomerization unit. This unit converts n-hexane to isohexane, which in turn can either be purified and sold as a solvent, or used as a blended stock for gasoline.

The additional processing costs associated with isomerization account for a portion of the current price difference between n-hexane and isohexane. Growing demand for isohexane will not eliminate these costs. Therefore, we feel isohexane will continue to be priced above n-hexane in the future, even if demand for isohexane ultimately exceeds demand for n-hexane.

Another major factor that needs to be considered regarding alternate solvents is product availability. The information shown previously in Exhibit B provides insight concerning the relative availability of these products. Because n-hexane occurs naturally in such large quantities, there is enough supply to accommodate substantial growth for this product. Unless unexpected regulations are imposed on the production or distribution of n-hexane, we can not envision a situation that would impose supply constraints on n-hexane.

Industry capacity for n-heptane is pretty well in balance with current demand, and new capacity could not be added quickly or inexpensively. If n-heptane were to become the solvent of choice for extraction of vegetable oil, there clearly would not be enough capacity to satisfy the demand. Since n-heptane appears unlikely to be an attractive alternative solvent for extraction of vegetable oils, this is probably a moot point.

Because current demand for isohexane is very small, solvent suppliers have had little reason to add production capacity for this product. We estimate that if all vegetable oil extractors were suddenly to convert from n-hexane to isohexane, solvent suppliers could currently supply only about 25% of the demand. Capacity to supply perhaps another 25% of your needs could be added fairly quickly. Beyond these levels, capacity additions would be more difficult.

While there is no question solvent suppliers could increase isohexane capacity, the proper incentives need to exist to encourage them to do so. As stated earlier, isohexane is already produced by refiners in fairly substantial volumes for use in gasoline blending. However, most refiners do not have the capability to extract and purify it for sale as a solvent. To retrofit refineries for capturing isohexane is both costly and time consuming, and refiners will not make these investments unless there are clear incentives for them to do so. Current demand clearly does not provide these incentives. Demand must will need to increase substantially to before capacity additions will occur.

In closing I'd like to summarize our observations about alternative vegetable oil extraction solvents. First, there appears to be no economic or operational incentive for vegetable oil processors to consider n-heptane as a replacement solvent. On the other hand, isohexane appears to have some operational advantages over n-hexane, and in some cases it may yield a higher quality oil. Therefore, it may represent an attractive alternative to n-hexane. Isohexane's big disadvantage is price, which is about 35% above n-hexane. While some of this price difference may diminish over time, it will not disappear completely since refiners must recover their isomerization costs. From a supply standpoint, there is not enough isohexane capacity to accommodate a sudden and massive switch to it. However, if a gradual conversion were to occur, solvents suppliers could add capacity to accommodate the increased demand provided there are appropriate incentives to so.

Exhibit A

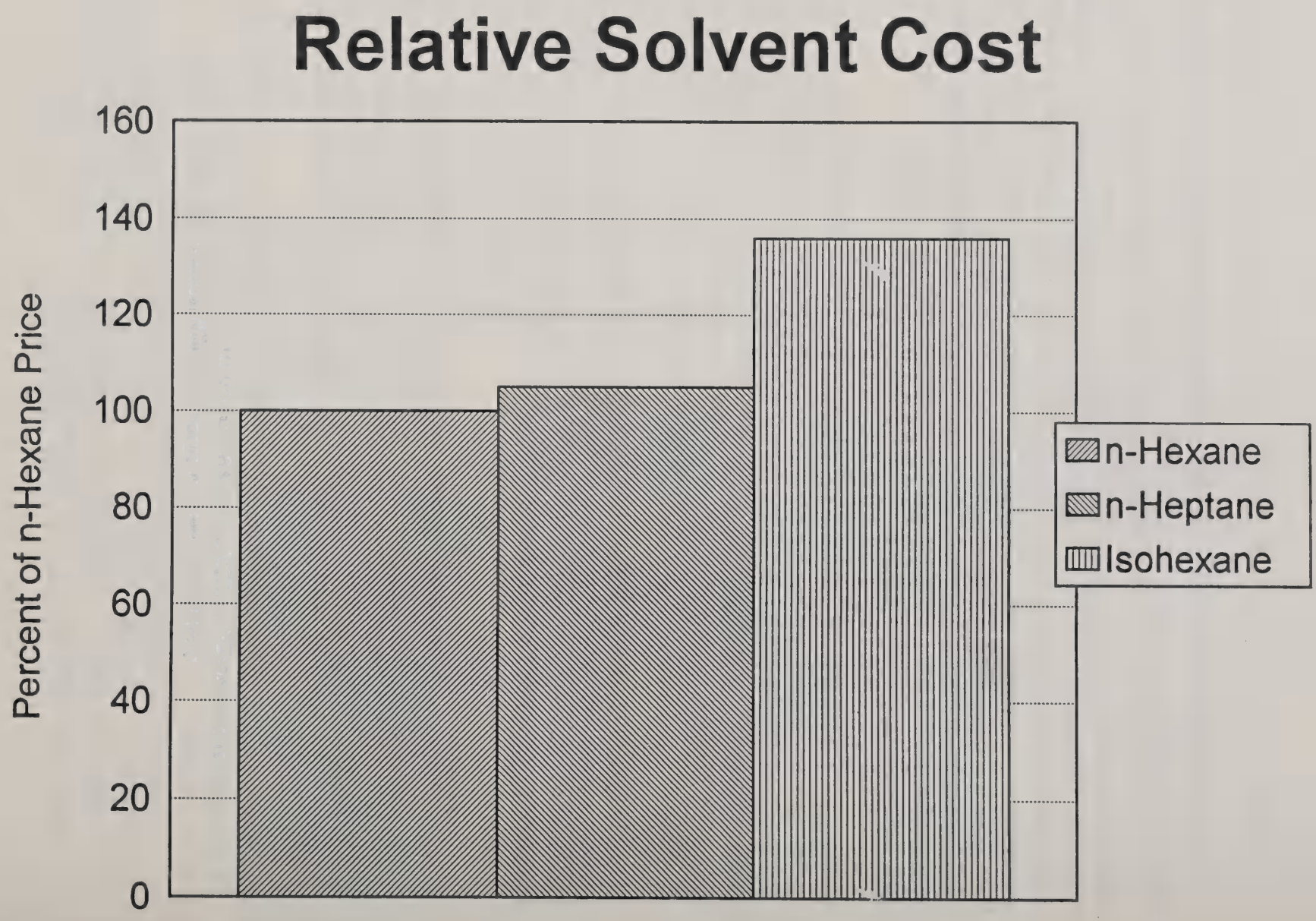

Relative Solvent Cost
Percent of n-Hexane Price
160
140
120
100
80
60
40
20
0
n-Hexane
n-Heptane
Isohexane

Exhibit B

Relative Market Size

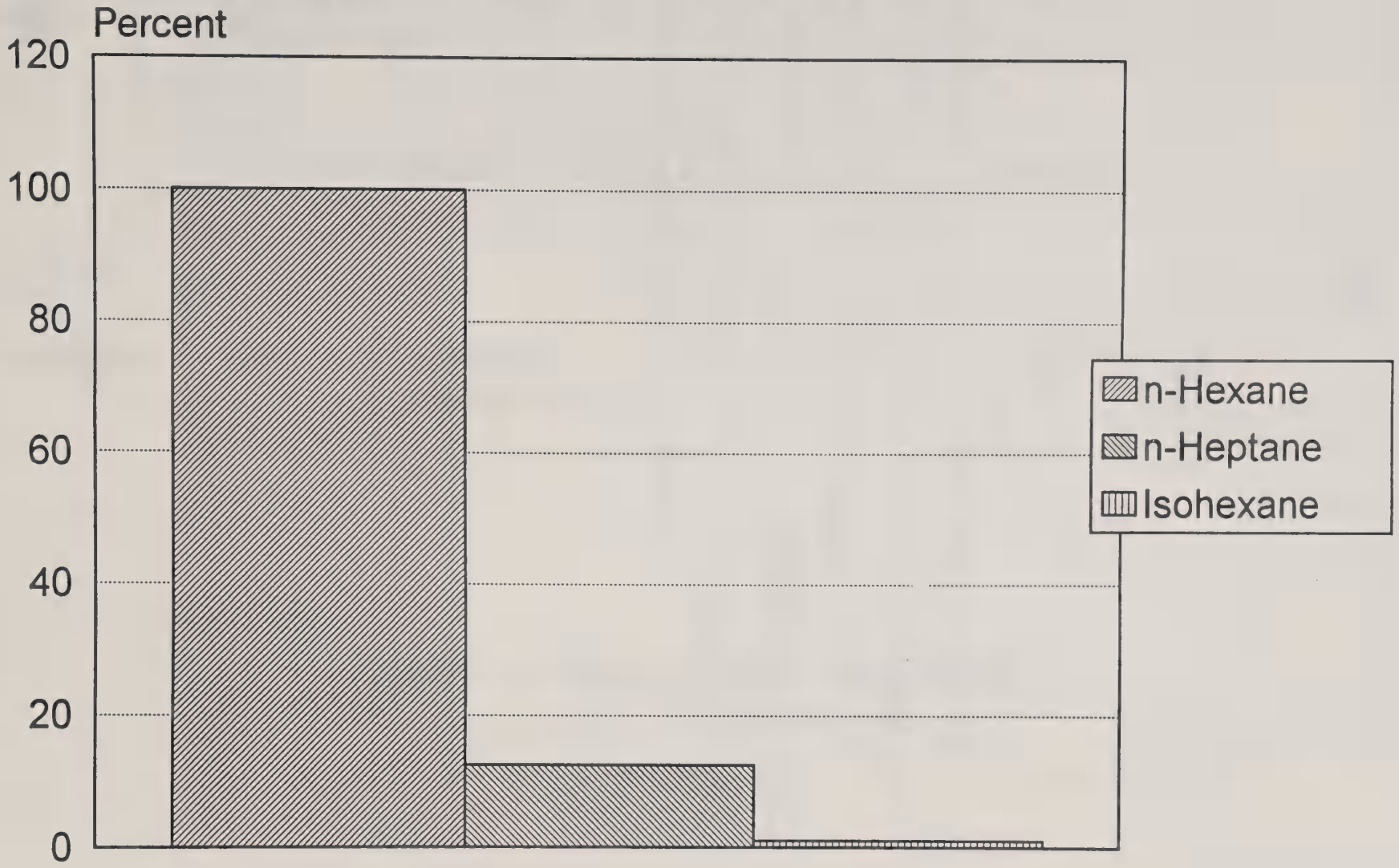
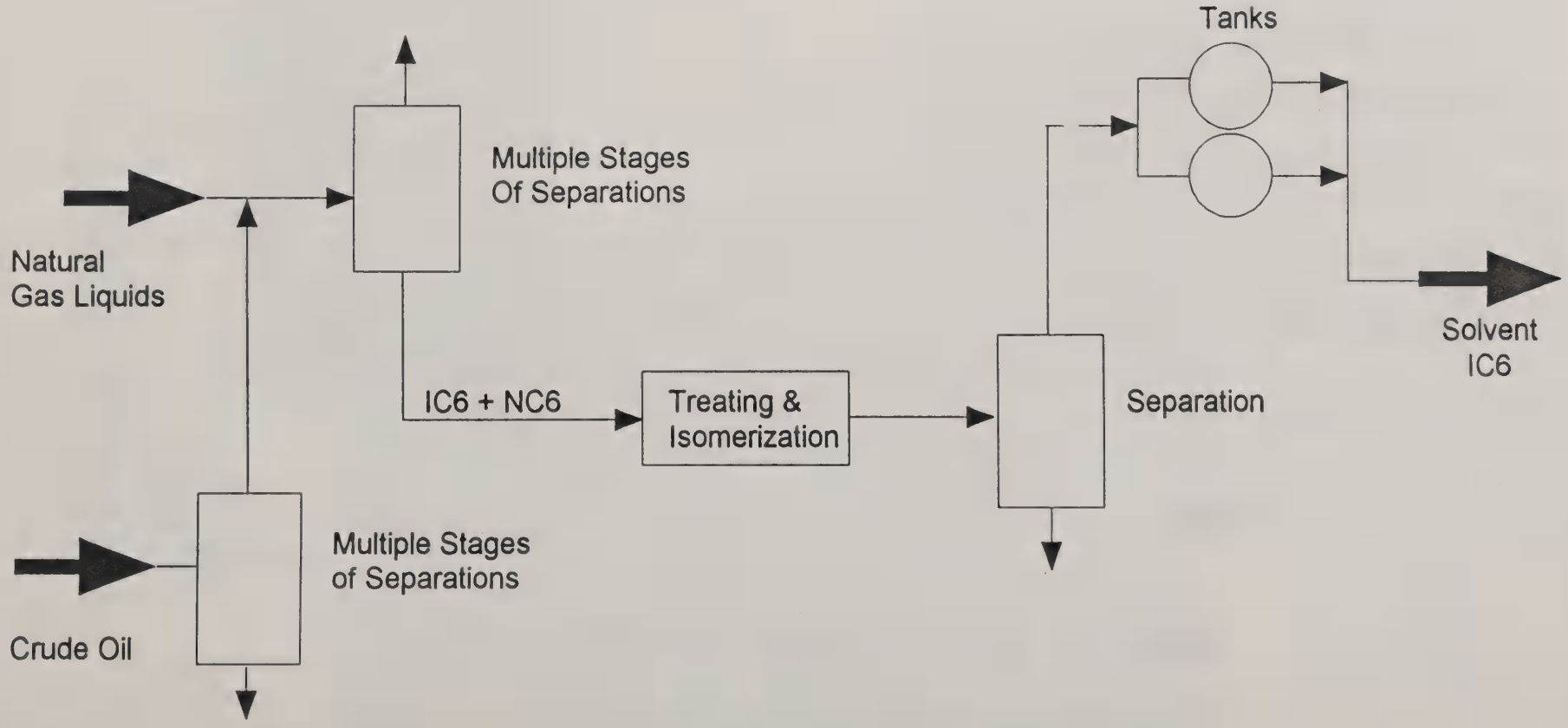


Exhibit C

PHILLIPS ISOHEXANE PROCESS



LIPOXYGENASE PATHWAY-DERIVED VOLATILE DEFENSE SIGNALS IN AFLATOXIGENIC ASPERGILLUS/COTTON PLANT INTERACTIONS

by

H. J. Zeringue, Jr.
ARS, USDA, SRRC
New Orleans, Louisiana

ABSTRACT

C_6-C_{10} alkenals, derived from fatty acids via activation of the lipoxygenase pathway, may function both as "volatile elicitors" and as "gaseous phytoalexins" in the cotton plant. C_6-C_{10} alkenals accumulating on damaged cotton plant tissues (e.g., damaged by fungal attack) were found to inhibit *Aspergillus flavus* and reduce aflatoxin contamination. Airborne signals consisting of individual C_6, C_7, C_8, C_9, and C_{10} alkenals in enclosed systems with developing cotton bolls were found to elicit the sesquiterpenoid naphthol phytoalexins, 2,7-dihydroxycadalene, and 2-hydrox-7-methoxy cadalene and their oxidation products lacinilene C and lacinilene C 7-methyl ether, together with the coumarin phytoalexin-scopoletin. These diverse alkenals may coordinate defense responses within the same cotton plant and even among neighboring cotton plants.

INTRODUCTION

Baldwin and Schultz (1) damaged leaves of potted poplar (Populous X euroamericana) ramet and sugar maple (Acer saccharum) seedlings and demonstrated increased concentrations of phenolic compounds in the damaged leaves and also in the leaves of undamaged plants sharing the same enclosure. Rhodes (2) found that Stika willow (Salix) trees attached by tent caterpillars (Malacosoma california pluviale) and nearly unattached control trees exhibited altered leaf quality. Fall webworms (Hyphantria cunea) fed the attached leaves grew more slowly than those fed leaves from unattached willows. Both references suggested that an airborne signal originating in damaged tree tissues may stimulate biochemical changes in neighboring undamaged trees that could influence the feeding and growth of phytophagous insects. We begin experimentation with volatiles involved in A. flavus host cotton plant interactions following those reported results on the possible importance of a host's plant defense system linked to an airborne signal.

RESULTS AND DISCUSSION

Zeringue (3) exposed cotton leaves for 7 days to volatile chemicals originating from A. flavus infected cotton leaves, A. flavus cultures or mechanically damaged cotton leaves. It was observed that volatiles from A. flavus - infected leaves triggered significant increases of 52 and 34% in phloroglucinol-reactive compounds (expressed as gossypol equivalents) in wounded or undamaged cotton leaves, respectively (Table 1). Bell (4) induced accumulation of phloroglucinol reactive compounds in tissues of cotton by inoculating with conidia of Verticillium alboatrum or with Sporangiospores of Rhizopus nigricans. He described the accumulation of these phloroglucinol- reactive phenolic compounds in terms of "gossypol equivalents" and discussed their accumulation relative to that of phytoalexin production. With the detection techniques utilized in this experiment, it was found that Heliocide H_2 (C_{25} terpenoid aldehyde, a natural cotton insecticide) was one of the predominant products formed in the volatile recipient (wounded) and (non-wounded) cotton leaves. Helicocides H_2 is formed naturally by a Diels-Alder addition of hemigossypolone and myrcene in the pigment glands of the cotton plant, Stipanovic and Bell (5). Zeringue and McCormick (6) found that myrcene represents 17.7% of the total volatiles in non-wounded Acala SJ-2 leaves and 24.8% of the total volatiles in wounded Acala SJ-2 leaves. Leaf damage caused by A. flavus penetration might release myrcene from the pigment glands, and by reacting with hemigossypolone, could increase the accumulation of Heliocide H_2 in the volatile-recipient leaves.

To study the effects of cotton leaf volatiles on A. flavus cultures, microbial free compressed air was passed continuously for 2- and 7-day test periods through enclosed systems containing wounded or nonwounded leaves of glanded or glandless cotton; the resultant emitted volatiles were bubbled through liquid

cultures of A. flavus, Zeringue and McCormick (6). After 2 days incubation, (Table 2) it was observed that volatiles from wounded glanded and wounded glandless cotton leaves retarded the growth of A. flavus. After 7 days incubation (Table 2) it was noticed that fungal growth was stimulated in cultures which received volatiles from wounded or non-wounded glanded cotton leaves, but not from either type of glandless cotton leaves. Wounding must release antimicrobial volatiles seen in both wounded SJ-2 and 8160 at 2 days. It also appears that the SJ-2 wounded and SJ-2 non wounded volatiles that stimulate the fungal growth at 7 days are being produced from the lysigenous pigment glands in the leaves since this stimulatory effect was not seen in cultures receiving volatiles derived from glandless 8160 leaves.

To explain these 2- and 7-day observations on A. flavus cultures, volatiles were trapped on Tenax collection tubes and volatile profiles were determined by Direct Injection/Gas Chromatography/Mass Spectral Analysis at 2- and 7-day periods, Zeringue and McCormick (6).

Over 90 compounds were identified by this method. Purified compounds of selected identified cotton leaf-derived volatiles were assayed in solid culture to determine which of volatiles were responsible for the bioactivity described above. Of the individual volatile components tested, C_6 - C_9 alkenals, especially trans-2-hexenal, exhibited the most inhibitory effects on the growth of fungus (Table 3). Note that stimulatory effects of the individual volatile components tested were not as pronounced as the inhibitory effects. Unbranched C_8, C_{12} - alkanals, 2- and 3-C_5 alkanones, α & β -pinene stimulated the growth of A. flavus.

These bioactive alkenals are cascade, breakdown products of the unsaturated fatty acids, linoleic and linolenic acids; their concentrations are greatly increased by mechanical damage of plant tissues, Lyr and Banasiak (7). The key enzyme for their biosynthesis is a membrane-bound lipoxygenase which is believed to be located both in chloroplasts and mitochondria, Sekiya et al (8), Mac Leod et al (9), Hatanaka et al (10). Because the akenals are highly inhibitory to A. flavus growth, they may be considered as "gaseous phytoalexins" because of their mode of production and antifungal effects.

Since C_6 - C_{10} alkenals are released from damaged cotton leaves, it seems logical to ask if these newly released volatiles could effect a defense expression in the same plant or in neighboring plants. In order to address this possibility, the following experiment was conducted. Microbial-free compressed air was designed to carry individual C_6, C_7, C_8, C_9, and C_{10}- alkenals and alkanals into enclosed systems containing artificially wounded and non-wounded Acala SJ-2 developing cotton bolls, Zeringue (11). Two days after treatment, discs were excised from the treated cotton bolls surfaces and were extracted to determine the induction of DHC, DHMC, LAC, LACME, and SCOP. Results indicated that all volatile alkenals tested produced elevated levels of the 5 induced phytoalexins in the artificially wounded developing cotton boll. All volatile alkanals tested produced

slightly elevated levels of SCOP in the artificially wounded cotton boll when compared to wounded controls. Wounding or tissue damage appears necessary for C_6 - C_{10} alkenals to function as active "volatile elicitors" for phytoalexin production.

These results demonstrate that C_6 - C_{10} alkenals may function both as "volatile elicitors" and as gaseous phytoalexins in the cotton plant. Air borne signals consisting of C_6, C_7, C_8, C_9 and C_{10} alkenals emitted from wounded cotton bolls or wounded cotton leaves can induce the production of the lacinilene, cadalene, and scopoletin phytoalexins on the carpel surfaces of the cotton bolls on the same plant or in bolls of nearly plants, Zeringue (11). It also has been demonstrated that tissue damage on the cotton leaf or the cotton boll such as that produced by invading fungi, can result in the production of the C_6 - C_{10} alkenals, "gaseous phytoalexins" which are fungitoxic to A. flavus. Volatile compounds appears to comprise a niche in the defense of the cotton plant and will comprise an area of research in which we will be very active in future experimentation.

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Table 1. Effects of volatile chemicals emitted by infected or wounded cotton leaves or by A. flavus cultures on the `gossypol equivalent' content of receptor cotton leaves after 7-days exposure.

Volatile source	Treatment condition means[1] in mμ mol `gossypol equivalents/g dry leaf tissue			
	Volatile receptor	Source leaves	Receptor leaves	Control leaves[2]
Cut leaves	Normal leaves	337 a[3]	225 b	197 b
A. flavus inoculated leaves	Wounded leaves	1003 c	702 c	337 d
	Normal leaves	481 e	339 f	225 g
A. flavus cultures	Wounded leaves		401 i	317 i
	Normal leaves		295 h	229 h

[1] There were at least three replicates of each treatment condition, and the data represent the means of the analyses of three subsamples in each treatment.
[2] Control leaves treated the same as receptor leaves, except they received only filtered compressed air.
[3] Means in separate columns in each treatment followed by the same letter are not significantly differed at P=0.05 according to Ducan's Multiple Range Test.

Table 2. Effects of two-and seven-day incubation of A. flavus in contact with cotton leaf volatiles.

Cotton cultivar	Dry weight as a percent of control
2 days	
8160 NW[1]	90.7 ± 9.1[3]
8160 W[2]	32.4 ± 8.6
SJ-2 NW	115.3 ± 6.7
SJ-2 W	32.4 ± 3.2
7 days	
8160 NW	100.6 ± 3.3
8160 W	96.6 ± 4.0
SJ-2 NW	179.3 ± 5.6
SJ-2 W	178.3 ± 1.9

[1] Nonwounded.
[2] Wounded.
[3] Standard error of mean of 3 separate experiments.

Table 3. Radial growth of A. flavus as a percent of control after two days in contact with some selected volatiles.

Volatile component	Level of tested Component (µl) 1	3	5	10	Concentration µM per tested µl
Alcohols					
3-methyl-1-butanol	91 ± 4[1]	88 ± 3	80 ± 6	55 ± 10	9.1
3-methyl-2-butanol	95 ± 6	95 ± 4	78 ± 3	80 ± 6	9.1
2-buten-1-ol	100 ± 3	100 ± 2	100 ± 3	100 ± 3	1.5
2-butoxy alcohol	96 ± 1	90 ± 1	86 ± 2	86 ± 3	7.6
1-pentanol	109 ± 2	100 ± 3	91 ± 2	90 ± 1	9.2
4-penten-1-ol	98 ± 2	98 ± 6	89 ± 5	89 ± 3	9.6
cis-2-hexene-1-ol	98 ± 2	93 ± 4	98 ± 6	98 ± 3	8.4
cis-3-hexene-1-ol	85 ± 2	80 ± 8	74 ± 5	69 ± 6	8.4
1-heptanol	136 ± 3	114 ± 5	73 ± 3	73 ± 4	7.0
3-hepten-1-ol	100 ± 3	89 ± 2	80 ± 4	73 ± 3	7.0
1-nonanol	136 ± 3	122 ± 3	128 ± 4	132 ± 3	5.7
1-decanol	96 ± 2	92 ± 2	91 ± 2	91 ± 5	5.2
Aldehydes					
hexanal	84 ± 5	76 ± 3	76 ± 2	0 ± 0	8.3
trans-2-hexenal	0 ± 0	0 ± 0	0 ± 0	0 ± 0	8.6
2,4-hexadienal	53 ± 3	0 ± 0	0 ± 0	0 ± 0	9.0
2-hexenal, diethylacetal	98 ± 2	0 ± 0	0 ± 0	0 ± 0	4.9
heptanal	67 ± 5	58 ± 3	49 ± 6	0 ± 0	7.4
trans-2-heptenal	82 ± 3	0 ± 0	0 ± 0	0 ± 0	7.6
octanal	114 ± 7	88 ± 5	50 ± 3	46 ± 3	6.5
trans-2-octenal	77 ± 3	0 ± 0	0 ± 0	0 ± 0	6.7
nonyl aldehyde	75 ± 4	60 ± 3	46 ± 3	0 ± 0	5.8
trans-2-nonenal	82 ± 2	0 ± 0	0 ± 0	0 ± 0	6.0
N-decyl aldehyde	96 ± 2	92 ± 8	91 ± 3	91 ± 3	5.3
dodecyl aldehyde	136 ± 5	112 ± 4	104 ± 3	104 ± 2	4.5
Ketones					
2-pentanone	133 ± 8	116 ± 3	116 ± 3	116 ± 5	9.4
3-pentanone	111 ± 3	121 ± 3	118 ± 2	116 ± 2	9.4
cyclohexanone	109 ± 6	107 ± 5	109 ± 3	91 ± 4	10.0
2-heptanone	80 ± 2	84 ± 2	76 ± 3	71 ± 4	7.1
3-heptanone	100 ± 1	96 ± 5	91 ± 4	91 ± 3	9.6
3-octanone	82 ± 4	82 ± 3	82 ± 1	82 ± 3	6.3
2-nonanone	94 ± 1	77 ± 2	77 ± 2	61 ± 3	5.9
Others					
myrcene	85 ± 5	90 ± 5	88 ± 3	86 ± 3	5.9
ocimene	95 ± 9	95 ± 3	88 ± 1	85 ± 2	5.8
limonene	90 ± 6	85 ± 3	83 ± 3	90 ± 3	6.1
camphene	131 ± 6	111 ± 5	111 ± 3	111 ± 2	6.2
α-pinene	114 ± 5	114 ± 4	114 ± 4	114 ± 1	5.9
β-pinene	114 ± 2	114 ± 3	114 ± 1	114 ± 2	6.3
caryophyllene	93 ± 2	93 ± 2	93 ± 2	93 ± 2	4.4
4-pentenoic acid	114 ± 3	108 ± 2	96 ± 3	86 ± 1	9.8
ethyl acetate	100 ± 4	95 ± 1	91 ± 4	86 ± 3	10.2

[1] Mean ± SD for 3 replicates/tested level.

PROGRESS IN IPA EXTRACTION[A]

E. W. Lusas, S. S. Koseoglu, K. C. Rhee, L. R. Watkins,
E. Hernandez, S.C. Doty and W.H. Johnson, Jr.
Food Protein Research and Development Center
Texas Engineering Experiment Station
Texas A&M University System
College Station, Texas 77843-2476
Phone: 409/845-2741; Fax: 409/845-2744

SUMMARY

Progress on development of a process for extracting cottonseed and soybean oils, with isopropyl alcohol (IPA) as the solvent instead of hexane, is summarized in this report. An alternative solvent is needed because of the high flammability of hexane, and because its major (45-95%) constituent (*normal*-hexane, CAS Number 110543) has been listed as a hazardous air pollutant in the 1990 Congressional Amendment to the Clean Air Act. IPA is a more polar solvent than hexane and has the potential of extracting additional water-soluble components, thereby increasing the burden on the refinery. Adjustments must be made in both oil extraction and refining processes. Further, energy requirements for IPA desolventization are 2.0-2.5 times greater/lb than for hexane, and heat conservation and recapture techniques are needed to narrow the operating cost differential.

Extraction with isopropyl alcohol-water azeotrope (IPAWA; 88% weight; 91% volume) and processing of the resulting oil were emphasized in the early part of this project. This is the fixed concentration at which IPA and water distills at a constant-boiling temperature until one component is exhausted , and is the form of IPA used by earlier researchers. However, the practical solvency of 65.6°C (150oF) IPAWA for cottonseed oil is only 10-15% by weight. Attention then turned to the use of high-concentration (93+%) IPA, referred to here as "HCIPA." When hot (71.1-76.7°C, 160-170°F), like hexane, it is totally miscible with oil in all proportions. This property had first been reported in 1950, but use of HCIAP had been put aside because of technical difficulties of recovery with the then available technology.

However, the recent development of pervaporation techniques may resolve this problem. IPA-water vapor condensates, collected from desolventization of extracted cottonseed and soybean marcs and from stripping of their miscella, were successfully concentrated from 85% to 97% IPA during the past year using a palletized pervaporation pilot line loaned by Texaco, Inc. The supplier, concerned about potential fouling of the membrane by short-chain fatty acids, has requested additional trials before recommending use of this equipment and estimating acquisition and operating costs.

[A]Presented at: 44th Oilseed Conference; USDA-ARS Southern Regional Research Center, New Orleans, LA, March 13-14, 1995.

Crude cottonseed or soybean oils, extracted by HCIPA, refined as well as those extracted by hexane. Swine and poultry grew as well on HCIPA- or hexane-extracted soybean meals after toasting to the 0.13-0.24 pH raise urease level. Techniques have also been developed to: 1) reduce the free gossypol content of cottonseed meal during processing; 2) partially remove oil from cottonseed using an (oil recovery cage-equipped) Hivex™ expander to reduce the amount of oil going to the extractor for solublization by solvent; and 3) obtain richer miscella, by additional extraction stages, to reduce the HCIPA:collet extraction ratio.

The research on extraction and processing of cottonseed oil is funded by a USDA-CSRS grant and the Texas Food and Fibers Commission. The American Soybean Association also is sponsoring a concurrent project to evaluate applicability of principles established with cottonseed to extraction and processing of soybean oil. Some data from the ASA project are included in this report to provide an overview of applicability of this technology to other oilseed oils.

BACKGROUND

Solvent extraction recovers substantially more oil than screw pressing, and is the leading domestic process for obtaining oil from cottonseed. The world's major extraction solvent is "hexane," a mixture of straight-, branched-, and cyclic-chain compounds with a narrow boiling range (about 65-69°C, 149-156°F) produced in the refining of petroleum. Some components of early industrial hexanes, including benzene, carbon tetrachloride and their derivatives, have been found toxic and have been eliminated from commercial use over the years. Hexane also is highly volatile and flammable, and presents a safety hazard long recognized by the extraction industry, with fires and explosions occurring occasionally.

The oilseeds extraction industry has long sought a less flammable solvent than the currently used commercial extraction hexane. The development of regional air emission standards and empowerment of regulatory agencies has made environmental issues an everyday concern for essentially every oilseeds processing facility in the nation. The 1990 Amendment to the Clean Air Act listed *normal*-hexane, a six carbon straight chain component, as a hazardous substance because of degenerative nervous disorders experienced in laboratory test animals. This compound is present in domestic commercial hexanes at levels of 45-95%. Toxicities of the other components of commercial hexane and their longer-chain homologs haven't been studied as extensively as *n*-hexane.

The composition of extraction quality "hexane" varies from manufacturer to manufacturer, and country to country. This categorical mixture essentially is the world's only solvent for edible oils extraction, and other feasible alternatives are not currently recognized. The history and status of various solvents have been reviewed by these and other authors (**1, 2**). Many solvents once used have been delisted over the years because of toxicological concerns. None of the non-flammable chlorinated solvents are encouraged or used any longer domestically. Research in Aqueous Extraction Processing, the use of hot water to extract oil, has had only limited success with oilseeds that contain high levels of phosphatides (**1**).

The only apparent bland "non-hexane" solvents eligible under current U.S. Food and Drug Administration regulations are alcohols -- ethyl alcohol (ethanol) and isopropyl alcohol (isopropanol, IPA). IPA was selected as the candidate alternative solvent for this project because of its higher

solubility for oil and fewer expected regulatory problems than ethanol, a regulated and taxed beverage. On occasional rechecking as this project has progressed, IPA still seems more promising.

Cottonseed was selected for probing this technology because it has the broadest technical challenges among the oilseeds -- including additional needs to inactivate or remove gossypol and aflatoxins, and opportunities for new added-value products. Findings in this project would be readily applicable to all oilseeds, and it has been endorsed by all of the domestic oilseed commodity groups. The American Soybean Association also has sponsored concurrent research at the Center on applying findings from the cottonseed research to soybean oil extraction and processing. Selected data from that project is enclosed to present similarities and contrasts between behavior of seeds and oils of different species.

IPA has been intermittently studied as an alternative solvent over many years. The two drawbacks to its use compared to hexane have been: 1) lower apparent solvency for oil; and 2) higher reclamation energy requirements. Much of the earlier IPA work was done 15 to 45 years ago in the era of low energy costs. In contrast, energy now is the second most expensive production input in oilseeds extraction after cost of the seed. The major objectives in alternative solvent extraction research today have become: 1) safety as recognized by the regulatory agencies; and 2) affordability of energy costs.

With the exception of occasional laboratory trials, earlier IPA extraction studies by most researchers were conducted using the water azeotrope of IPA (IPAWA). Figure 1 (**3**) shows the vapor-liquid composition and boiling points of IPA-water mixtures. With application of heat, the temperature of an IPA-water mixture will rise until a minimum constant boiling point of 176.6°F (80.2°C) is reached. The temperature will then remain constant until one of the constituents is exhausted by evaporation, after which the temperature will rise rapidly to the boiling point of the remaining constituent. The distilled IPAWA has a fixed composition of 87.8:12.2, IPA:water, weight:weight (or 91.3:8.7, IPA:water, volume:volume) and a specific gravity of 0.8180 at 20°C (69°F) (**3**).

Until recently, it has been expensive and technically complex to rectify IPA above the "88%" level. Hexane is completely miscible with oil in all proportions, IPA (actually IPAWA) is miscible with water but has limited solubility for oil. Solubility may be further reduced by dilution with water absorbed from the material being extracted, depending on water availability. But, there is at least one advantage. Solubility is temperature-dependent and enables the chill-separation of oil and solvent at lower energy cost than the recovery of IPA by distillation. Thus, at least part of the recovered, previously-used, solvent might be recycled for extraction (**4, 5, 6, 7, 8, 9**).

IPAWA requires 2.58 times more energy per pound for evaporation than hexane (Table 1). Although the miscella can be chill-fractionated, the hold-up solvent adhering to the marc can only be recovered by evaporation. Also, sufficient oil-free solvent must be generated for the final extraction stage. Partial recovery of the solvent by evaporation or other means is required in any continuous process.

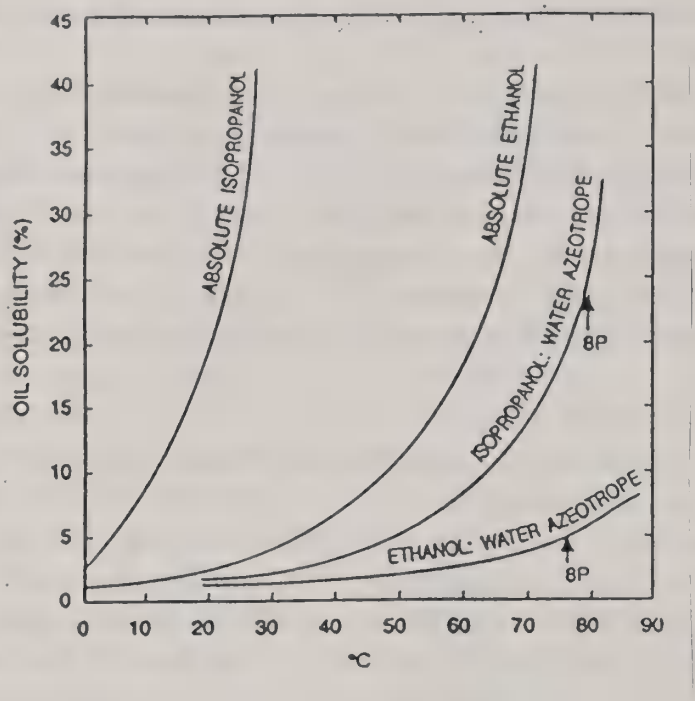

Figure 1. Vapor-liquid composition and boiling points, isopropyl alcohol-water (3).

Table 1. Characteristics of Hexane and IPAWA Solvents and Their Performance. From Sullivan et al. (10), with modifications.

CHARACTERISTIC	HEXANE	IPA AZEOTROPE, "IPAWA"
Oil Solubility	Completely miscible.	Miscible at high temp. Immiscible at low temp.
Water Solubility	Immiscible	Completely miscible
Flash Point, TCC	< 0°F	64°C, 147.2°F
Boiling Point (760 mm Hg)	68.7°C, 156°F	IPAWA = 80.2°C, 176°F 95% IPA = 81.5°C, 179°F 100% IPA = 82.4°C, 181°F
Heat of Vaporization	144 BTU/lb	IPAWA = 371 BTU/lb 95% IPA = 322 BTU/lb 100% IPA = 288 BTU/lb
Azeotrope	5% Water	12% Water
Spec. Gravity: 15.6°C, 60°F 25°C, 77°F 20°C, 68°F	0.674 — —	IPAWA = 0.816 IPAWA = 0.815 IPAWA = 0.8180 95% IPA = 0.7995 100% IPA = 0.7863
Pounds/gallon, 25°C, 77°F	5.60	6.83

RESEARCH PROGRESS

Reduction of Oil in Collets by Hivex Expander:

An Anderson International Company Hivex (with an oil removal cage) was used to reduce the oil content of cottonseed collets before the IPA extractor. With proper conditions (premoistening the seed to 12-14% moisture content, and tempering to 54.4 or 82.2°C, 130 or 180°F) before flaking and expanding, 40-50% of the oil in fully-dehulled cottonseed could be removed at the expander cage. When properly made, the collets extracted to less than 1% residual oil content with IPAWA (88% isopropanol). However, care had to be taken to ensure porous, extractable collets when working with minimum residual hulls. Hard "bullet-like" collets, with greatly-reduced extractability, apparently occurred with either inadequate denaturation (cooking) of the seed protein or when discharged from the expander at too low a temperature to expand. While this technique appeared to work well for dehulled cottonseed (with ca. 35% oil), it was not possible to remove significant amounts of oil from dehulled soybeans (containing about 22% oil).

Reducing the oil content in collets by about one-half before going to the extractor theoretically reduces solvent requirements by about one-half. However, the IPAWA miscella from the extractor contained only about 12-15% oil, compared to about twice that amount when extracting with hexane. The need for twice the solvent for the remaining oil essentially off-set the gains at the drainage cage, but still left us with a more energy-intensive process than hexane. Our attention then turned to improving the oil-solubilization properties of IPA, and specifically to extraction with HCIPA.

Solubility Curves of Oils in Concentrated IPA:

Figure 2F shows temperature solubility curves of crude cottonseed and soybean oils. In developing the curves, IPAWA at essentially its boiling point (176.6°F, 80.3°C) was supersaturated with equally hot, previously extracted, crude cottonseed or soybean oils. Oils contents of the miscellas (upper phases) after equilibration at predetermined temperatures were determined. For a yet unexplained reason, the solubility of soybean oil has consistently been higher in our research than that of cottonseed.

Although Figure 2F indicates that at a 1:1 w:w IPAWA:collet ratio and 76.7°C (170°F) we should obtain a miscella containing 16% crude oil, only 12% was achieved. This led to the work of Harris and Hayward (11), who in 1950 had concluded that the maximum feasible cottonseed oil concentration in IPAWA miscella is 10% at 155°F. They (11) also had recognized that hot IPA, at concentrations over 93%, is completely miscible with cottonseed oil at all proportions and extracts less carbohydrates than IPAWA. This has been reverified in our trials, and the implication is that it may be possible to establish conditions where IPA extracts as much oil as hexane. Figure 3 shows that, at 170°F (76.7°C), 60% PBSY (prime bleachable summer yellow) cottonseed oil is completely miscible in IPAs of 93% or higher concentration. Figure 4 shows that 60% RBD (refined, bleached, deodorized) soybean oil is completely miscible in IPAs at 91% or higher.

However (Figures 3 and 4), the use of HCIPAs also results in higher residual oil contents in the chill-separated upper (IPA-rich) phase. It also results in higher IPA contents in the (oil-rich) lower phase, requiring more energy for solvent removal. A compromise is achieved when 95% IPA is

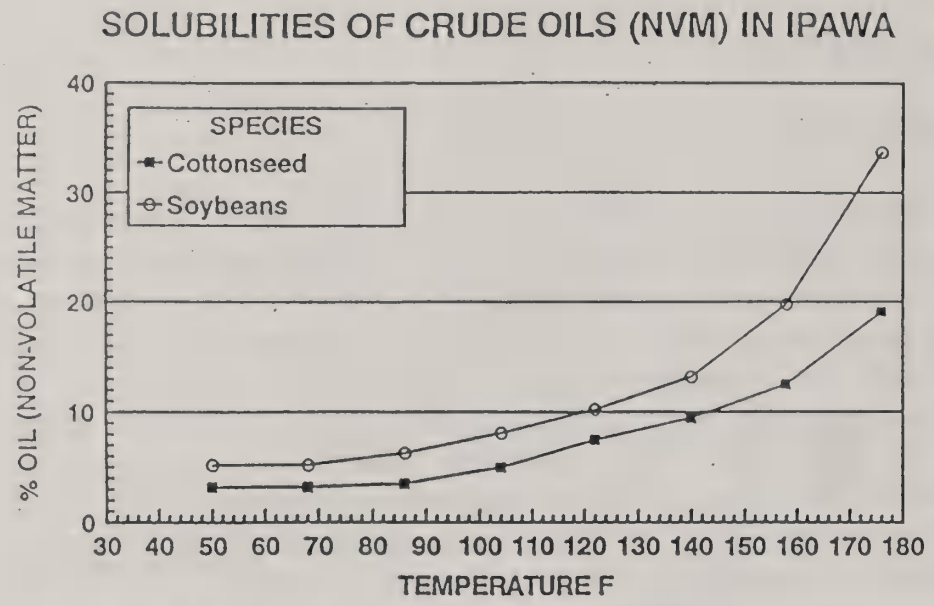

Figure 2F. Solubilities of crude soybean and cottonseed oils (NVMs) in isopropyl alcohol-water azeotrope. (IPAWA = 87.8:12.2 IPA:water, w:w:; 91:9 IPA:water, v:v; constant boiling 176.6 F (80.3 C).

selected. Figures 3 and 4 also suggest that the higher solvencies for RBD soybean oil compared to PBSY cottonseed oil are due to differences in the oils themselves -- possibly the higher polyunsaturation and lower melting point of soybean oil, since lecithins and other co-products in the crude extracted oils are no longer present.

Figure 5F (from last year) shows that the last few degrees are critical to getting maximum extraction of crude cottonseed oil when using 95% IPA as the solvent. Figures 6 and 7 show chill-separated miscellas containing as much as 90%:10% IPA:water w:w solvent. Concentrations of over 60-70% oil in the miscella resulted in higher residual oil contents in the upper phases for both cottonseed and soybean oil.

Counter-Current Extraction Profiles:

A potential means for reducing the amount of IPA solvent needed is by obtaining miscellas richer in oil content. A profile of a 9-stage counter-current simulated extraction, using a 1:1 ratio of 96% IPA and cottonseed collets made on an Anderson International Solvex Expander (without an oil removal cage) is shown in Figure 8. "Stage 1" is the first exposure of the collets to extraction, and has the highest oil content accumulated from prior counter-current extractions. Miscellas with over 48% crude cottonseed oil were obtained by keeping solvents and collets hot. As would be expected, oil in the marcs and miscellas decreased with successive extraction stages. However, the increased hold-up of IPA in the marcs with successive extractions was unexpected in view of earlier observations that both collets and IPAWA result in less hold-up (about 24-30%) compared with flakes and hexane.

These observations are corroborated by the profile of a 9-stage counter-current simulated extraction of soybean collets handled in the same fashion (Figure 9), in which an exit miscella with 38% soybean oil was obtained. The addition of more stages should be possible in designing new extractors and rebuilding older models, and doesn't increase the solvent requirements of the process.

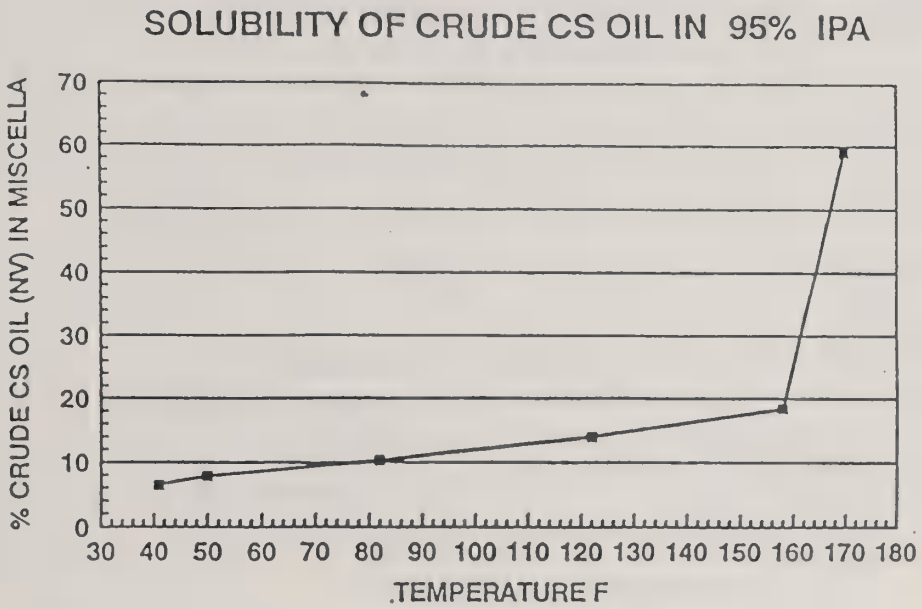

Figure 5F. Solubility of 60% crude cottonseed oil (n.v.) in 95% IPA.

As mentioned earlier, the solvency of IPA can be reduced by absorption of moisture from the material extracted. Figure 10 (from last year) shows the relative ability of IPAs of different concentrations to dry Hivex Expander-processed collets (in 1:1 solvent:collet ratio). Presumably, interpolations can be made between the approximately parallel lines. If the objective is to conduct the extraction at 93% or higher IPA content, in theory, the processor should be able to select any combination of collet and IPA moisture levels that will equilibrate to less than 7%. This information was applied successfully in pilot plant trials this year to compensate for varying moisture levels in dried collets. However, the relationships shown in Figures 3 and 4, where extraction with IPA concentrations higher than 95-97 indicate reduced chill-separation of oil into the lower phase, and increased retention in the upper phase, bear further monitoring.

On chill-separating 95% IPA miscellas of crude cottonseed and soybean oils, partitioning does not become apparent until about 104°F (40°C). The neutral oil favors partitioning into the lower oil phase (Figures 11 and 12, respectively, and the phosphorous (indicative of lecithins) into the upper IPA phase (Figure 13). In the current trials, we did not see as much partitioning of free fatty acids into the IPA phase as with past IPAWA extractions. This is probably due to the fact that 95% IPA is far less polar than 88% IPA, and therefore less of an attractant for free fatty acids.

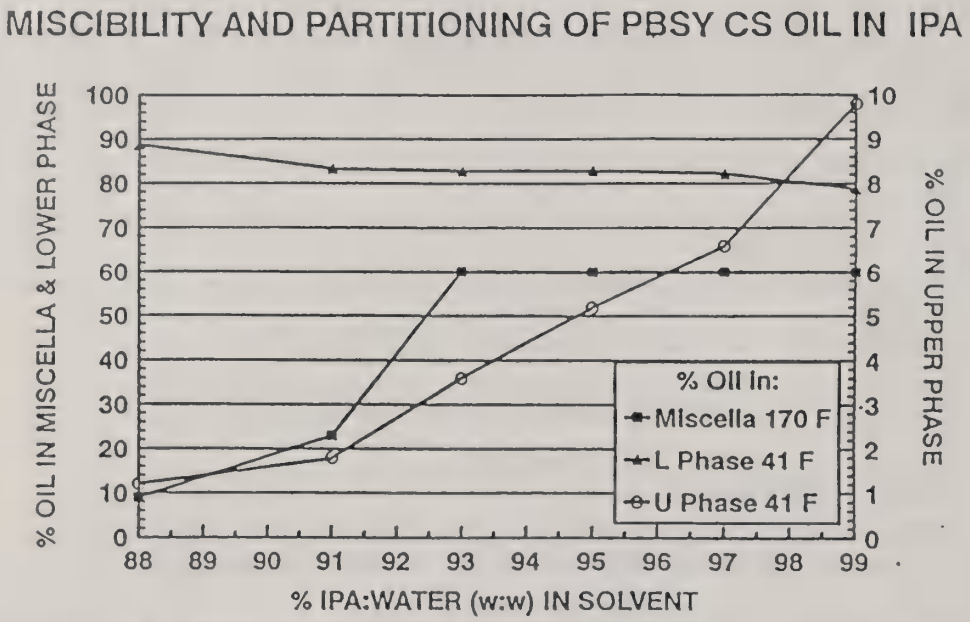

Figure 3. Miscibility and partitioning of 60% PBSY cottonseed oil in IPAs of different concentrations.

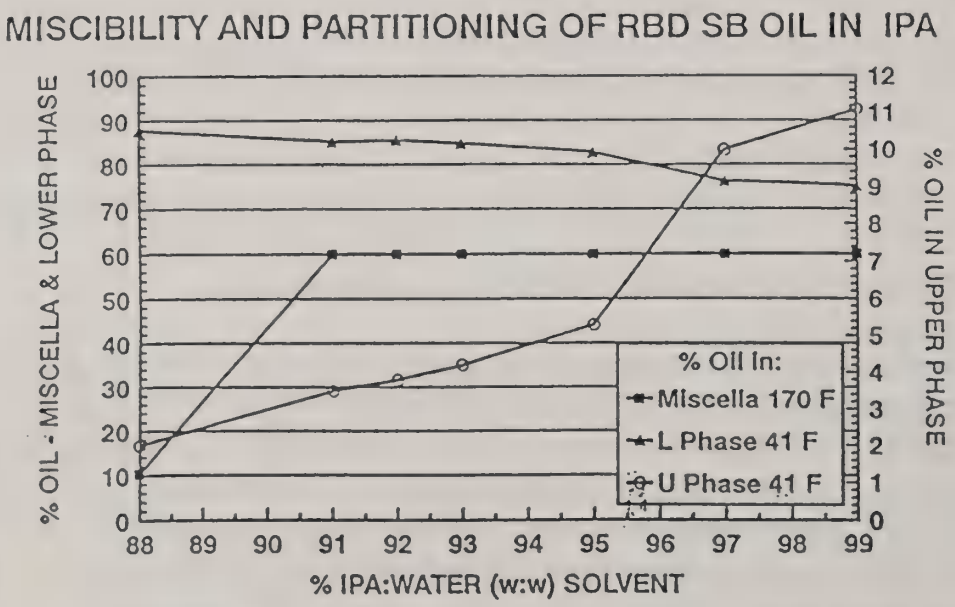

Figure 4. Miscibility and partitioning of 60% RBD soybean oil in IPAs of different concentrations.

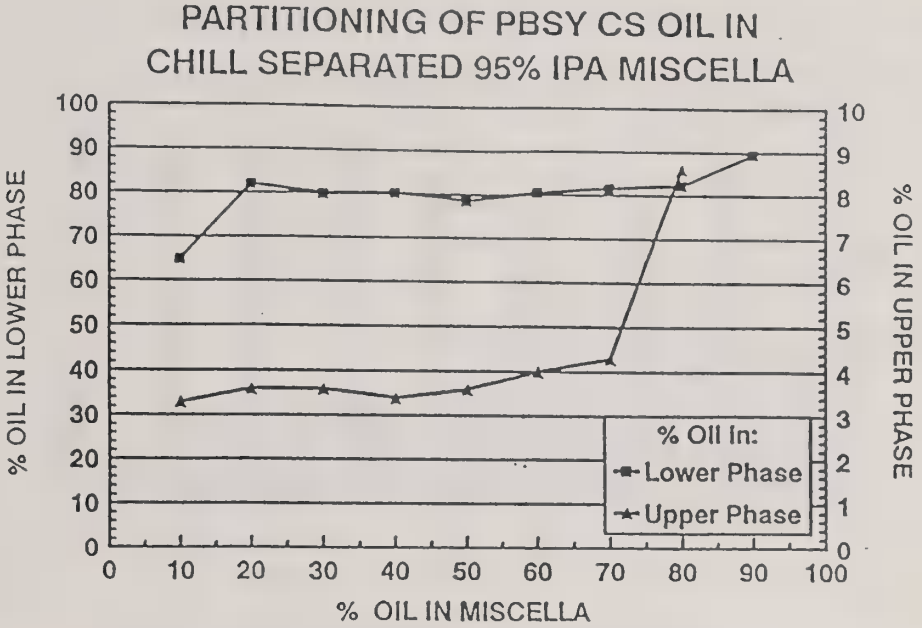

Figure 6. Oil contents in upper and lower miscella phases. PBSY cottonseed oil completely solubilized in 95% IPA w:w at 170 F, then chill-separated at 41F (5 C).

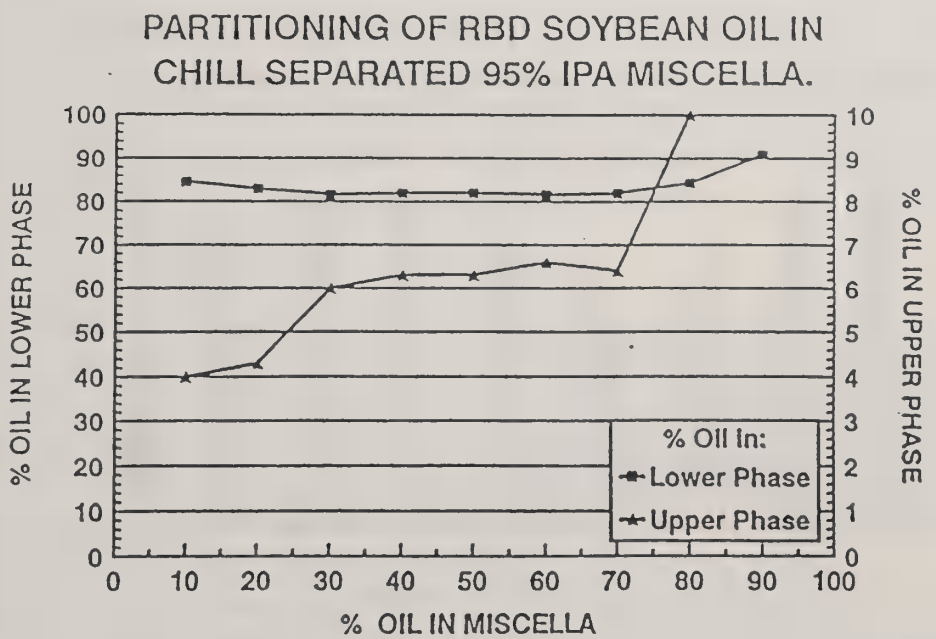

Figure 7. Oil contents in upper and lower miscella phases. RBD soybean oil completely solubilized in 95% w:w IPA at 170 F, then chill-separated at 41 F (5 C).

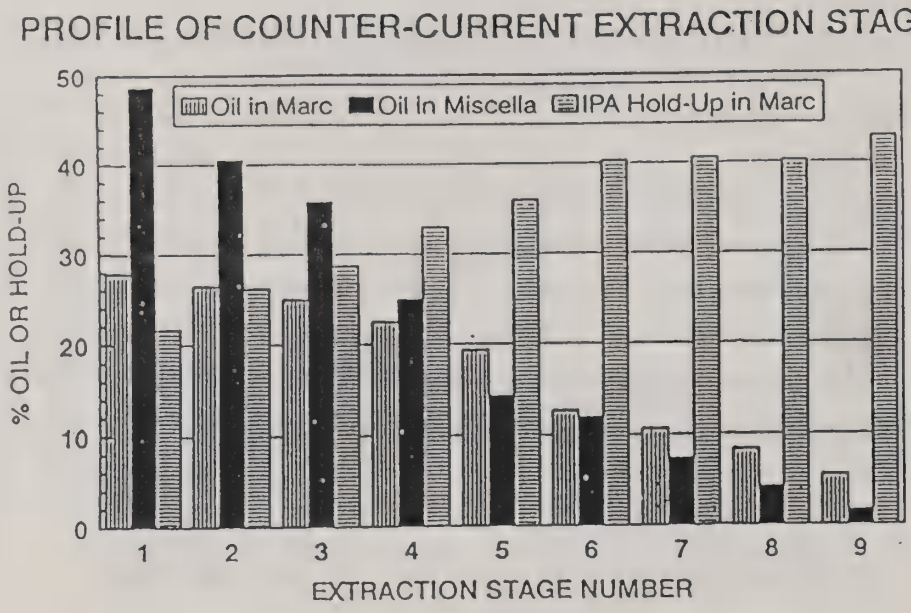

Figure 8. Oil contents of marcs and miscellas, and IPA hold-up, in 9 counter-current extraction stages of cottonseed collets made by Anderson Solvex Expander (TM) (without drainage cage). Initial oil content 34.4% at 4.5% moisture; 95% IPA (w:w); 1:1 solvent:collet ratio; 170 F (77 C).

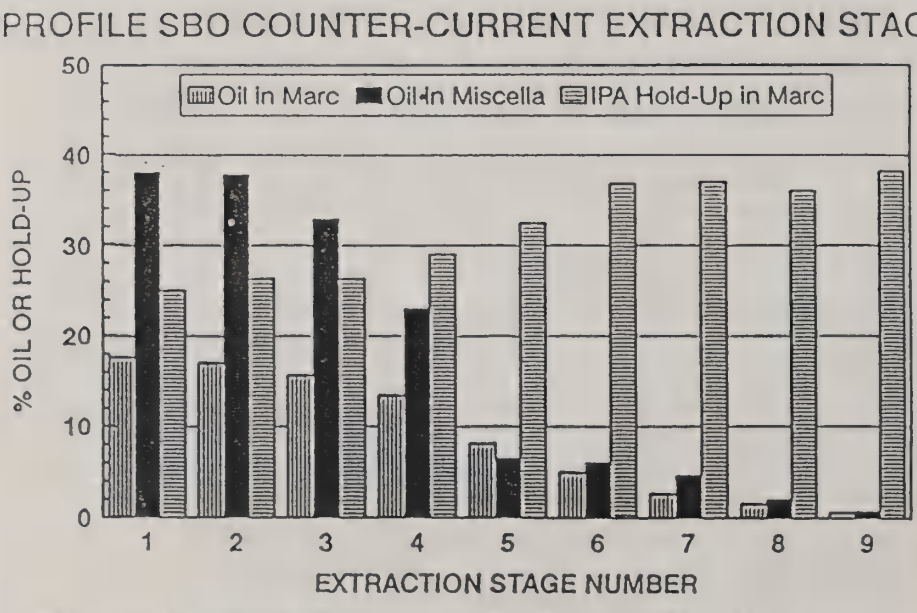

Figure 9. Oil content of marcs and miscellas, and IPA hold-up, in 9 counter-current extraction stages of soybean collets made by Anderson Solvex Expander (TM). Initial oil content 24.4%; 4.0% moisture; 95% IPA (w:w); 1:1 solvent collet ratio, 170 F (77 C).

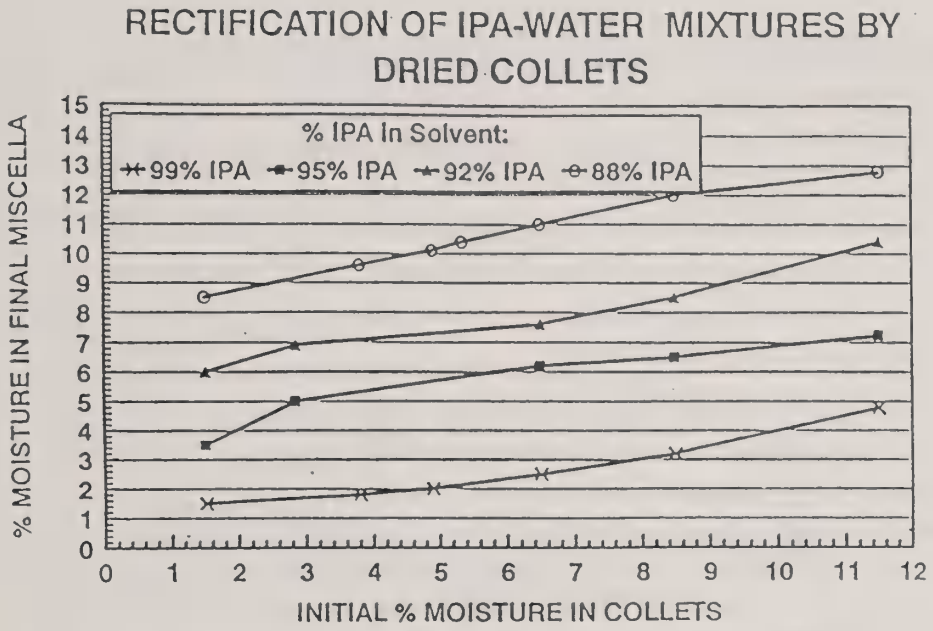

Figure 10. Abilities of dried Hivex Expander processed cottonseed collets to rectify various IPA-water mixtures; 1:1 solvent : collet ratio, w:w.

Gossypol in Cottonseed Products:

The reduction of free gossypol in cottonseed meal to "poultry grade" levels (a maximum of 450 ppm total, or 10 ppm per protein percentage) is expected to broaden its use and improve its economic value. Various techniques were tried early in the project to reduce free gossypol content in meal, including extruding cottonseed collets in the expander, holding them hot for a selected period, and reexpanding before solvent extraction. However, IPA extraction itself has been found effective in binding gossypol.

In a small pilot plant trial, meats were dehulled and separated from fuzzy cottonseed by an IMPCO decorticator. Moisture content was adjusted to 12% and the seed equilibrated for 12 hrs. The lot was then split. One-half of the conditioned seed was heated to 180°F (82°C), flaked to 0.012 in, expanded at 220-230°F (104-110°C), and dried to 4.5% moisture. This treatment was labeled: "1-Pass Collets." The other half was cold-flaked to 0.015 in, extruded through a Solvex Expander at 190-200°F (88-93°C) with enough added steam to flash off at 12% moisture residual, and held in an insulated container for 30 min. The temperature at the end of the holding period was 162°F (72°C). The collets were reexpanded at 220-230°F (104-110°C) and dried to 4.5% moisture content. This treatment was labeled: "2-Pass Collets."

Both treatments were extracted with 95% IPA, 1:1 ratio, 170°F (77°C) in a 9-stage counter-current extraction simulation. Analyses are shown in Table 2.

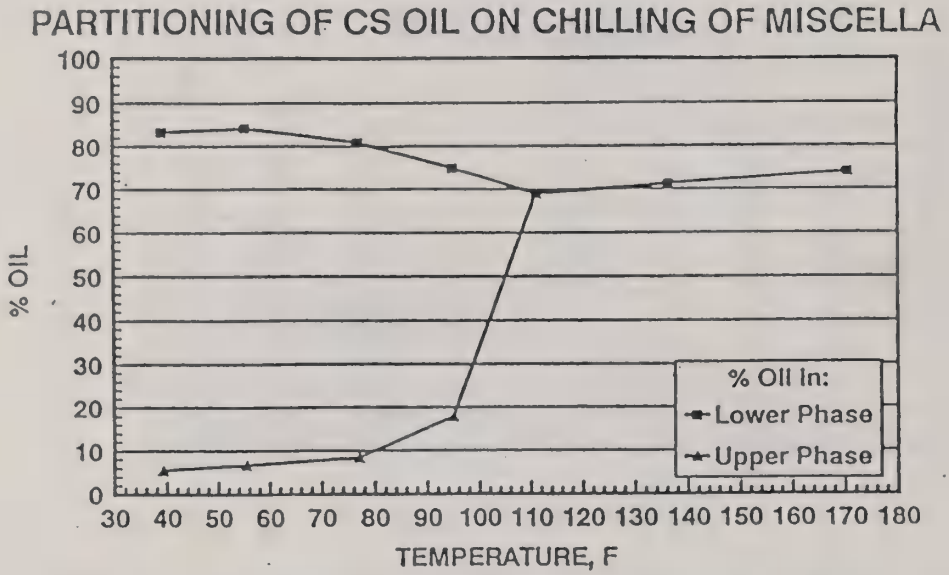

Figure 11. Distribution of crude cottonseed oil in upper (IPA) and lower (oil) layers with cooling. Extracted from Solvex collets, 1:1 solvent:collet ratio; 95% IPA (w:w); 170 F (77 C).

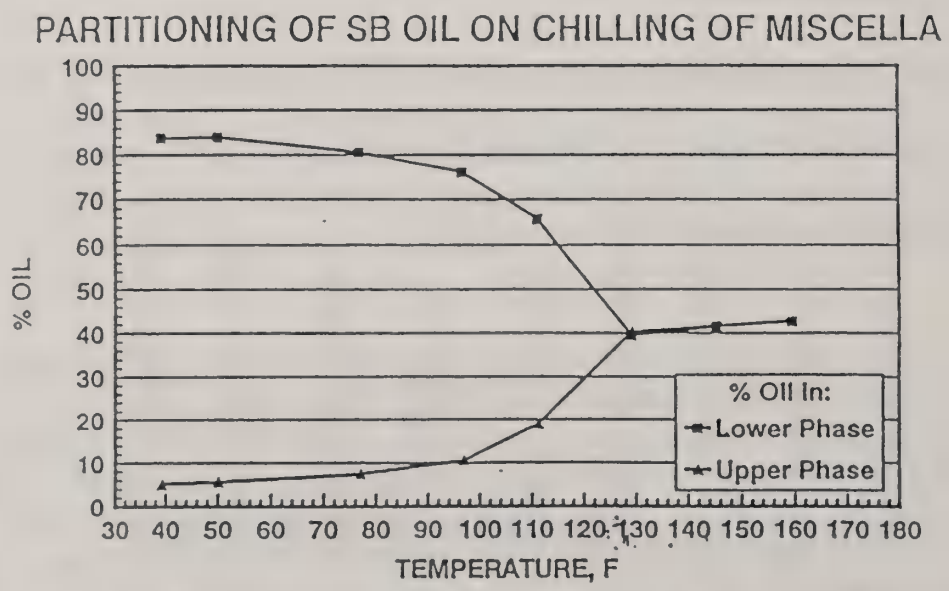

Figure 12. Distribution of crude soybean oil in upper (IPA) and lower (oil) layers with cooling. Extracted from Solvex collets, 1:1 solvent:collet ratio; 95% IPA (w:w).

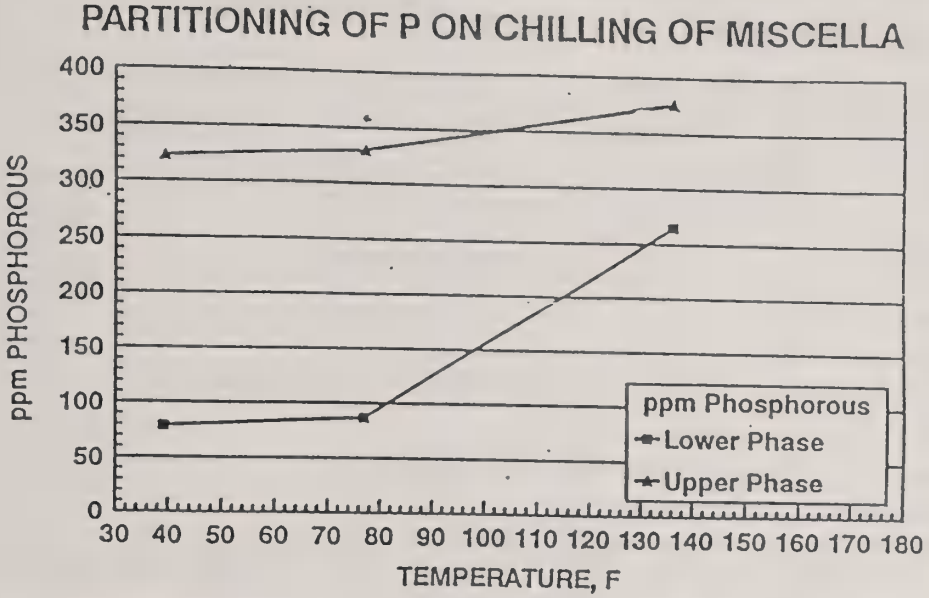

Figure 13. Distribution of phosphorous in upper (IPA) and lower (oil) crude cottonseed oil miscella layers with cooling. Extracted from Solvex collets, 1:1 solvent:collet ratio; 95% IPA (w:w); 170 F (77 C).

Table 2. Changes in the free gossypol contents of one- and two-pass Solvex-expanded cottonseed collets during 95% IPA extraction. The meals have not yet received heat during desolventization or toasting.

MATERIAL	FREE GOSSYPOL	TOTAL GOSSYPOL
DEHULLED MEATS	1.043 %	1.262 %
ONE-PASS COLLETS		
Before Extraction	0.1064	1.170
After 9th Stage Extraction	0.0515	1.755
Extracted Crude Oil	—	0.105
TWO-PASS COLLETS		
Before Extraction	0.0616	1.179
After 9th Stage Extraction	0.0211	1.633
Extracted Crude Oil	—	0.136

Decreases in free gossypol content during the 9 extraction stages are shown in Figure 14. The experiment shows that, with the assistance of moisture and heat at the expander, free gossypol is controllable to very low levels in cottonseed meal and oil with HCIPA extraction.

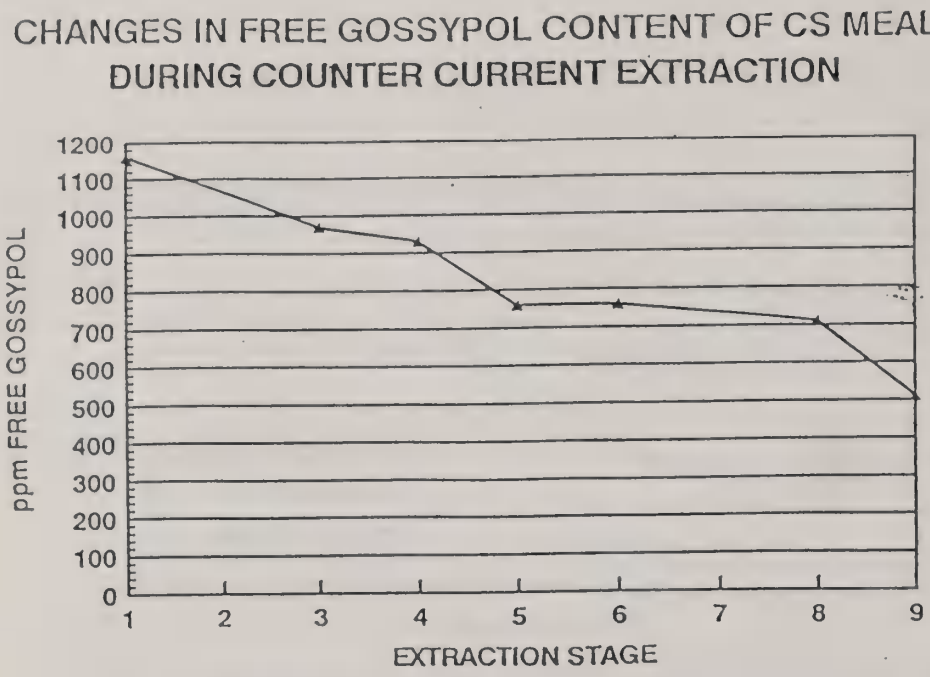

Figure 14. Changes in free gossypol of one-pass Solvex-expanded cottonseed collets, 9-stage counter-current simulation.

Pilot Plant Trials:

Pilot plant extraction trials have been made with cottonseed and soybean collets using 96% HCIPA, essentially a 1:1 solvent:collet ratio, a 6 in wide Crown Model 2 7-stage extractor, and 170°F (77°C). Miscellas containing 27-28% crude oil were obtained with both oilseeds. After chill-separating at 41°F (5°C), the bottom layers were desolventized using a Luwa thin film evaporator. The resulting crude oils behaved normally in alkali refining, bleaching and deodorization, and produced RBD oils well within current industry practices. The described cottonseed extraction and oil refining trials were conducted with Hivex-extruded collets, and the soybeans with Solvex-extruded collets. Extraction trials also are in progress with Solvex-extruded cottonseed collets.

Processing of 9-stage HCIPA-Extracted Cottonseed and Soybean Oils:

Approximately 5 gallons each of crude cottonseed and soybean oils were obtained by chilling miscellas from the 9-stage extraction simulation to 4°C (39°F) and separating by decanting. The soybean miscella separated into an upper solvent phase containing 5.53% oil, 244 ppm phosphorous and 0.31% FFAs, while these values for the oil phase were 83.21%, 368 and 0.63, respectively. The lower phase was desolventized in a rising film evaporator at 15 psig vacuum. The crude soybean oil was degummed in the laboratory by hydrating it with 1.5% deionized water for 0.5 hr and centrifuging at 10,000 rpm for 15 min. It was not necessary to alkali refine the degummed soybean oil because of its low free fatty acid content. Cottonseed oil was refined using 0.3% excess caustic solution and washed with deionized water at 82°C (180°F). The washed oils were dried and vacuum-bleached, using 0.4% Filtrol 105 for the soybean oil and 1.0% for the cottonseed oil. Then, 1,800 g of each bleached oil was deodorized in the laboratory at 240°C (464°F), 6 mm Hg for 3 hr. Mid-process and final analyses are shown in Table 3.

Table 3. Analyses of processed, 95% IPA-extracted, cottonseed and soybean oils.

Product	FFA (%)	P (ppm)	PV (meq/ 1000 g)	Color
Soybean Oil				
Crude	0.35	485	—	—
Degummed	0.08	—	—	—
Refined	0.020	—	—	—
Bleached	0.026	0.0	0.0	0.2R 1.6Y
Deodorized (with citric)	0.046	0.0	0.0	0.1R 0.4Y
Cottonseed Oil				
Crude	0.65	334	—	—
Refined	0.03	—	5.18	3.4R 44Y
Bleached	0.022	—	1.19	1.2R 10Y
Deodorized (with citric)	0.026	0.0	0.0	0.9R 5.3Y

Commercial lecithins are fractionated using different types and concentrations of alcohols. Samples of crude lecithins, from degumming of HCIPA- and hexane-extracted soybean oils were sent to industry laboratories with the objective of determining if IPA altered the ratios of phosphatides extracted. An extraordinarily large phosphatidic acid content was reported, but may have been due to microbial or enzymatic degradation during processing and shipping. This trial will be repeated.

Feeding Trials of Hexane- and HCIPA-Extracted Soybean Meals:

To resolve possible concerns that HCIPA-extracted meals might be less nutritious (have greater essential amino acid damage) than hexane-extracted meals, two 1,400 lb. lots of dehulled soybean meal were extracted with the respective solvents, toasted, and compared in weaned pig and chick battery feeding trials. With minimal heat treatment during desolventization, HCIPA- and hexane-extracted meals had urease activities of 1.98 and 1.04 pH units rise, respectively -- a level considered indicative of excessive trypsin inhibitor activity in feeding monogastric animals. This was further corroborated by Protein Dispersibility Indexes (PDIs) of 64.43 and 22.01, respectively. Trypsin Inhibitor values were: raw soybeans -- 672.35 TIU/mgN, HCIPA-extracted soybean meal -- 434.78 TIU/mgN, and hexane-extracted soybean meal -- 179.66 TIU/mgN.

The samples were adjusted to 20% moisture, heated at 18 psi (12-20 min) until they showed "trace activity" in the SoyChek rapid assay, and dried at about 100°F. Urease activities of the resulting products and commercial soybean meal from an often used source were: HCIPA- extracted "toasted" soybean meal -- 0.24 pH rise, hexane-extracted "toasted" soybean meal -- 0.13 pH rise, and commercial soybean meal -- 0.17 pH rise. PDIs were: HCIPA- extracted "toasted" soybean meal -- 14.05, and hexane-extracted "toasted" soybean meal -- 12.56. No significant differences in animal growth were found between the two meals in 200 pig 26 day growth tests and in chick battery growth tests. The soybean meal growth tests are of special significance, since possible effects of residual gossypol (as might occur in feeding cottonseed) are not of concern.

Recovery of High Concentration IPA:

The advantages of working with HCIPA as an extraction solvent are clear. Pervaporation -- a new membrane separation technique -- has been developed in the European biotechnology separations industry and shows promise for rectification of alcohols and acetone to concentrations above their azeotropic distillation levels. As shown in Figure 15, the mixture to be separated is passed across a cross-flow membrane. The feed is gaseous or superheated liquid and the material to be separated (smaller molecules, in this case water) permeates the membrane in vapor form under slight pressure into a vacuum area where it is exhausted or condensed. The concentration of IPA from 86:14 w:w mixtures with water to over 99% purity has been repeatedly demonstrated **(12)**.

Figure 16 shows the principle in more detail. The solvent-oil miscella, or dilute aqueous solutions of IPA, are heated and only the water-IPA vapors are taken to the pervaporation system. Oil and the co-products of solvent extraction do not get near the pervaporation membrane, thus avoiding fouling which occurs with other membrane separation processes.

Reportedly, pervaporation membranes will separate vapors if available. However, permeation of liquids requires heat for evaporation, in turn cooling the unpermeated feed. This is then returned to a heater for superheating and recycled over the pervaporation membrane (Figure 17). Heat of vaporization to permeate the membrane is required only for the small fraction of the mixture that passes through the membrane. If 87.8% IPAWA vapors are sent to the pervaporation membrane, and 95% IPA is desired, about 7.2% water must be removed by pervaporation.

A matter of special concern is how to handle IPA vapors, including those mixed with air and noncondensable gases. In the case of hexane vapors, a mineral oil scrubber is used. We have proposed to evaluate mineral oil scrubbers, but will also consider aqueous vapor-scrubbing systems like that shown in Figure 18 and cold surface contact condensers.

An integrated distillation/pervaporation process for recovering oil and recycling HCIPA might look like the flow sheet in Figure 19. As with other modern plants, considerable use must be made of heat recapture systems to minimize net energy input. Pervaporation systems have been developed in Europe for recovery of acetone, ethanol and isopropyl alcohol, and for their concentration.

A palletized pervaporation system was loaned to the Center by Texaco, Inc. IPA:water condensate, recovered from cottonseed and soybean meal and oil desolventization was successfully concentrated from 85% to 97% purity. However, the supplier wants to further check the process and determine whether distilled short-chain fatty acids might foul the membrane. Additional trials will be conducted during the next several months to answer this question and enable estimation of pervaporation system installation and operating costs.

Needs for odor control to meet environmental regulations have lead to the development of various air scrubbing and vapor condensation systems in recent years. Suppliers of vapor recovery systems have been contacted. Light-weight mineral oil, as used for scrubbing non-condensable gases in hexane extraction systems, also will be evaluated for IPA recovery, although currently it is thought that a more polar solvent -- or possibly water -- might be better for this purpose.

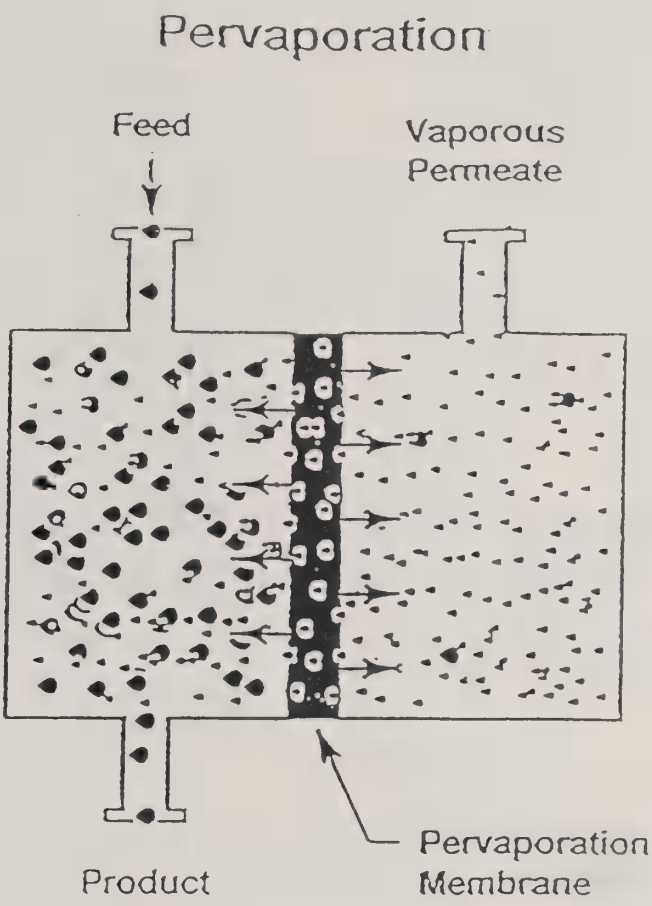

Figure 15. Schematic of feed in cross-flow pervaporation (12).

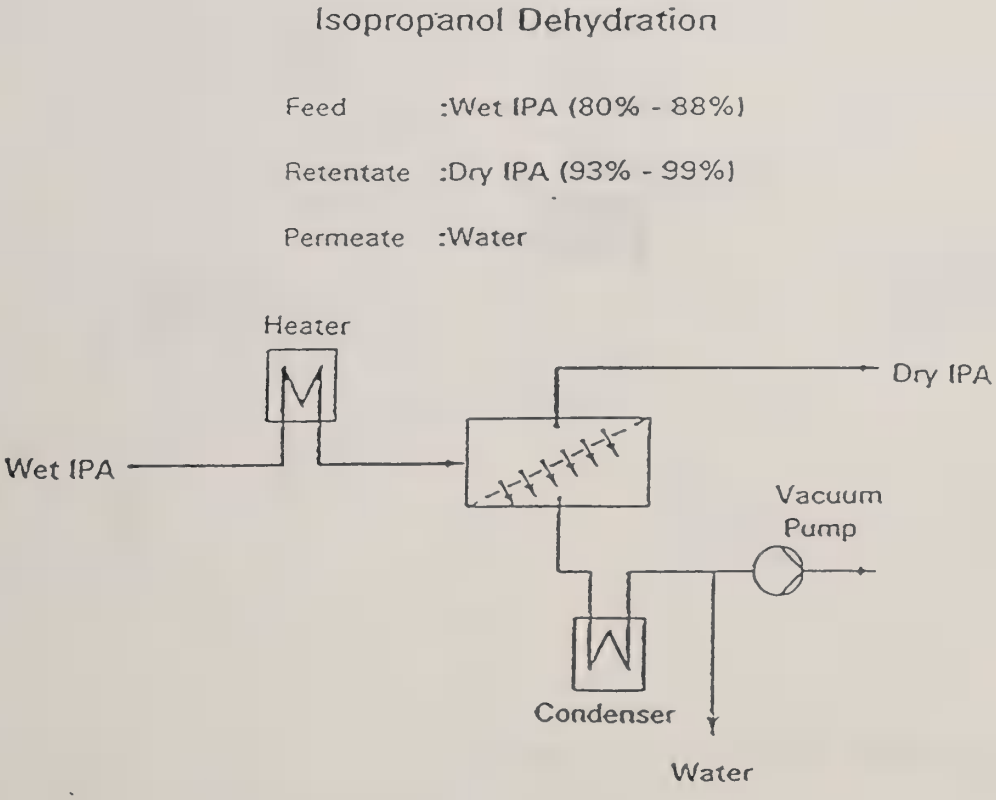

Figure 16. Schematic pervaporation IPA dehydration process (12).

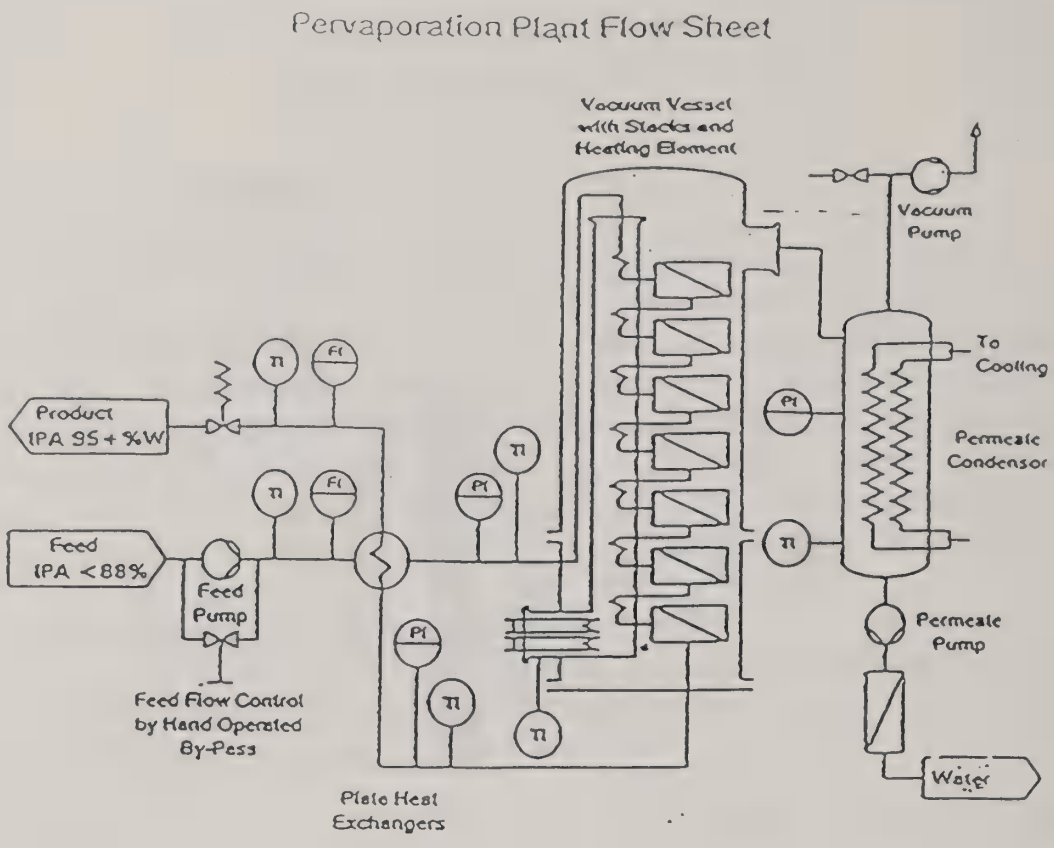

Figure 17. Pervaporation plant flow sheet. (FI = flow indicator; PI = pressure indicator; TI = temperature indicator (12).

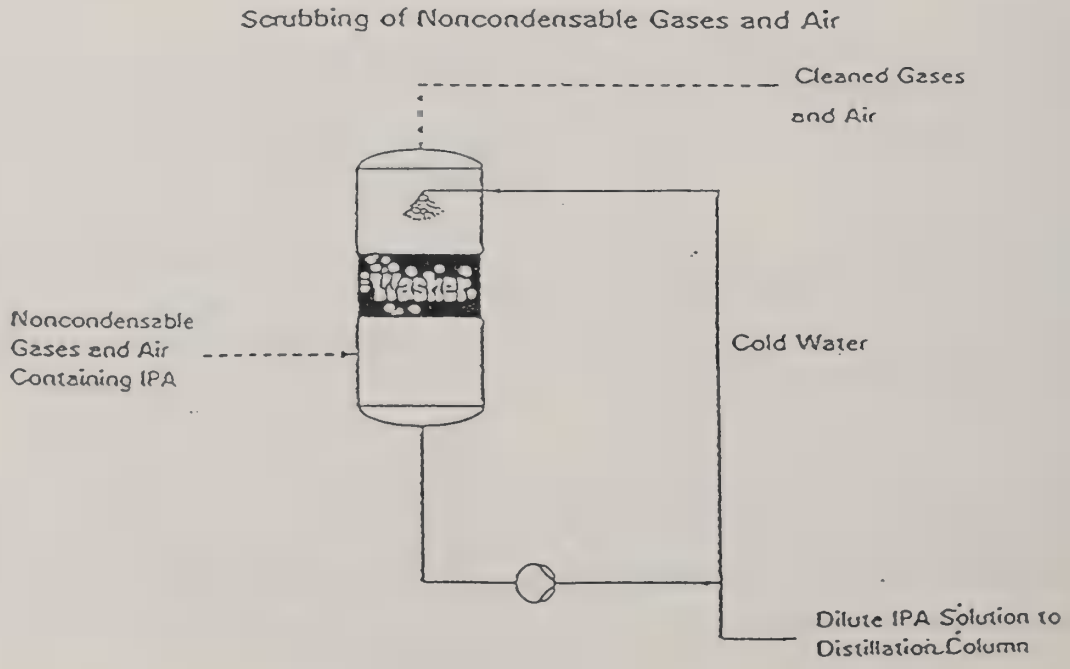

Figure 18. Tentative scrubber for recovering IPA from noncondensable gases and air (12).

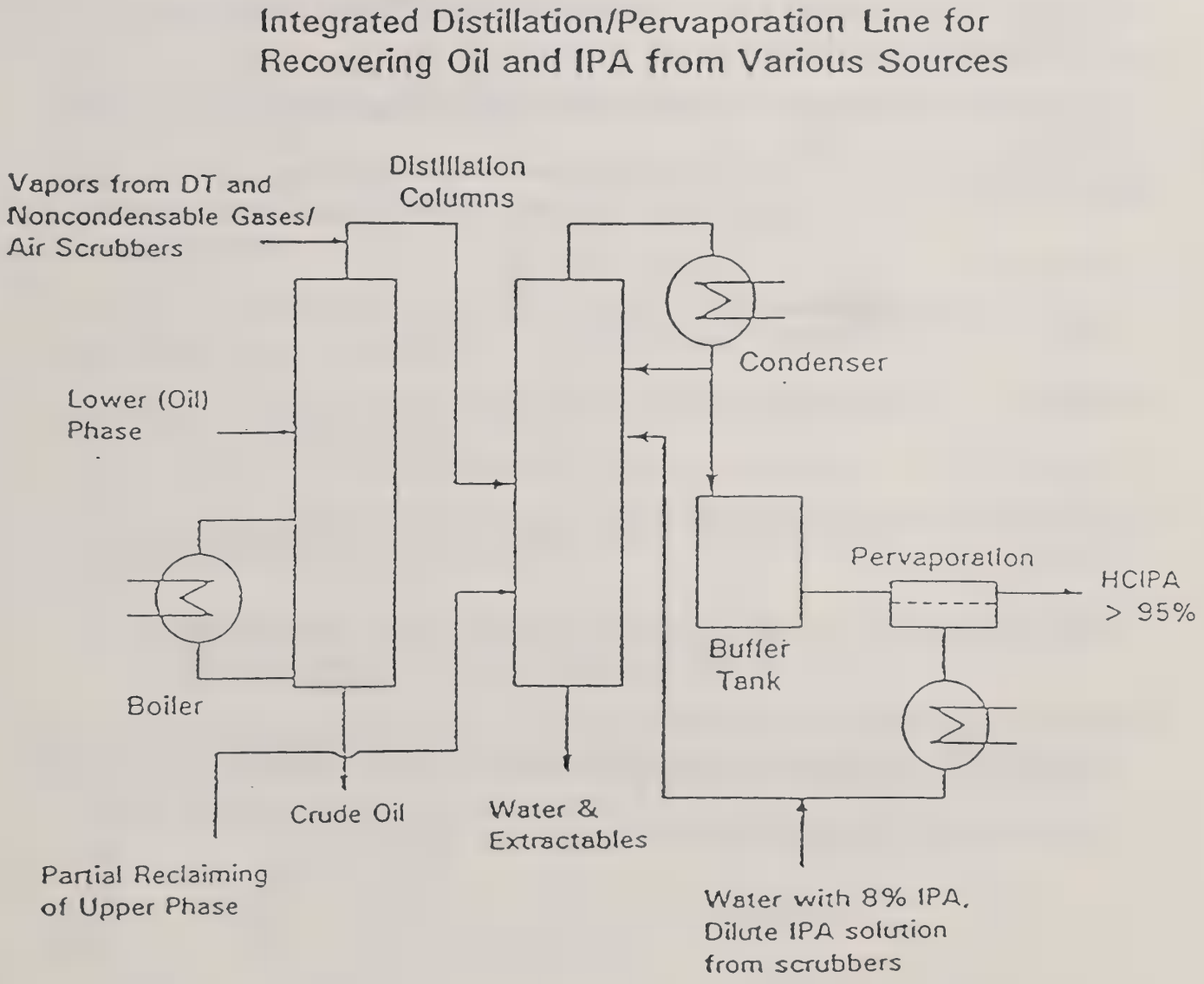

Figure 19. Tentative integrated distillation/pervaporation process for recovery of oil and HCIPA (12).

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